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STUDIES IN THE SYSTEM $CaO\text{-}Al_2O_3\text{-}SiO_2\text{-}H_2O$ IV; PHASE EQUILIBRIA IN THE HIGH-LIME PORTION OF THE SYSTEM $CaO\text{-}SiO_2\text{-}H_2O$*

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ABSTRACT

Phase equilibria in the high-temperature portion of the system $CaO\text{-}SiO_2\text{-}H_2O$ were determined by the use of hydrothermal quenching techniques. Three previously unidentified phases, designated X, Y, and Z, having the probable compositions $8CaO\cdot 3SiO_2\cdot 3H_2O$, $6CaO\cdot 3SiO_2\cdot H_2O$ and $9CaO\cdot 6SiO_2\cdot H_2O$ were found to be stable to temperatures above 800° C. at moderate water pressures. *X*-ray diffraction patterns, optical properties and infra-red absorption spectra were obtained, and are diagnostic for the various phases.

The equilibrium temperature for the reaction $C_8S_3H_3$** $=\alpha' Ca_2SiO_4$ (bredigite) $+CaO+H_2O$ increases from 820° C. at 2000 psi to 870° C. at 15,000 psi. The curve for $C_6S_3H=\alpha' Ca_2SiO_4+H_2O$ ranges from 790° C. at 7,500 psi to 810° C. at 15,000 psi; and the reaction $C_9S_6H=$ rankinite $+H_2O$ varies from 807° C. at 2000 psi to 820° C. at 15,000 psi. C_3SH_2 is in equilibrium with $X(C_8S_3H_3)+Ca(OH)_2$ at 505° C. at 10,000 psi and 520° C. at 15,000 psi. Afwillite decomposes at about 215° C. at 15,000 psi.

X is apparently a calcium analogue of chondrodite (Taylor, personal communication), and a related phase X* formed from compositions near the C_2S ratio at low pressures may be another member of the chondrodite-type series. Attempts made to synthesize members of the chondrodite series in the $MgO\text{-}SiO_2\text{-}H_2O$ system for comparison were largely unsuccessful. Possible applications of the results to the study of cement materials and mineral associations are discussed.

INTRODUCTION

The stability relationships of phases in the system $CaO\text{-}SiO_2\text{-}H_2O$ have been important to mineralogists and cement chemists alike for many years; and, while a great deal of the work done in the past has been concerned with equilibria under atmospheric conditions, newer techniques in recent years have made possible more extensive investigations at elevated temperatures and pressures. The present study has been di-

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** Throughout the paper the customary cement chemists' abbreviations $C=CaO$, $S=SiO_2$, and $H=H_2O$ are used for the molecular formulae of the compounds.

rected toward obtaining information on the stability relations of calcium silicate hydrates under hydrothermal conditions. It was hoped that new data obtained under conditions of higher pressure and temperature at which equilibrium is readily attained would indicate the ultimate direction in which lower temperatures non-equilibrium reactions tend to proceed. The high-lime portion of the system was selected, inasmuch as phase equilibrium data in this region could eventually give information leading to the understanding of the behavior of cement clinker components such as $3CaO \cdot SiO_2$ and $2CaO \cdot SiO_2$ under conditions of hydration, and of the natural hydrous and anhydrous mineral counterparts.

While the total composition of hydrated cement is high in CaO content, tobermorite (ideally $4CaO \cdot 5SiO_2 \cdot 5H_2O$) or poorly crystallized structurally related hydrates are now believed to form the basis of the binder in concrete and high-temperature insulating materials (Taylor, 1950, 1952; Kalousek, 1954, 1955). A summary of conditions of formation, properties, and apparent stabilities of various lime-silica hydrates has been given by Bogue (1955, Chap. 22), Bernal (1952), Taylor (1952_a), and Kullerud (1953), and a list of properties by Heller and Taylor (1956). It would appear from these data and from the work of Flint, McMurdie and Wells (1938) and of other recent investigators that in the high CaO portion of the system the minerals afwillite, hillebrandite, foshagite, possibly a high-temperature hydrate (such as $C_2SH(D)$) corresponding to the $2CaO:SiO_2$ ratio, and C_3SH_2 would be stable in the "hydrothermal" range. A systematic study should yield more accurate information on the stability limits of these phases.

Buckner and Roy (1955) in their study of the join $CaSiO_3$-H_2O found that tobermorite of the $CaO:SiO_2$ ratio 1:1 was stable as high as 220° C. at 15,000 psi water pressure, and that an intermediate phase was formed for a small interval (40° C.) above this temperature before giving rise to the less hydrous phase xonotlite. Recently the stability relations of dicalcium silicate and related compositions were determined under hydrothermal conditions (Roy, 1958. In press). The present study was directed toward obtaining information on hydrates in the high-lime portion of the system CaO-SiO_2-H_2O and as such is an extension of the previous study to lower temperatures. Of particular interest was the determination of the upper stability limits of hydrated phases where they are in equilibrium with anhydrous compounds such as rankinite, larnite or bredigite.

A composition diagram of a portion of the ternary system on which are plotted most of the well established phases is given in Fig. 1, and naturally occurring minerals are given by name. Cross-hatched lines are drawn to suggest solid solution; the variation in H_2O content and $CaO:SiO_2$ ratio in the tobermorite series is described in detail by Taylor (1950, 1952_a, 1952_b). Compositions from $3CaO \cdot 2SiO_2$ to $3CaO \cdot SiO_2$ were in-

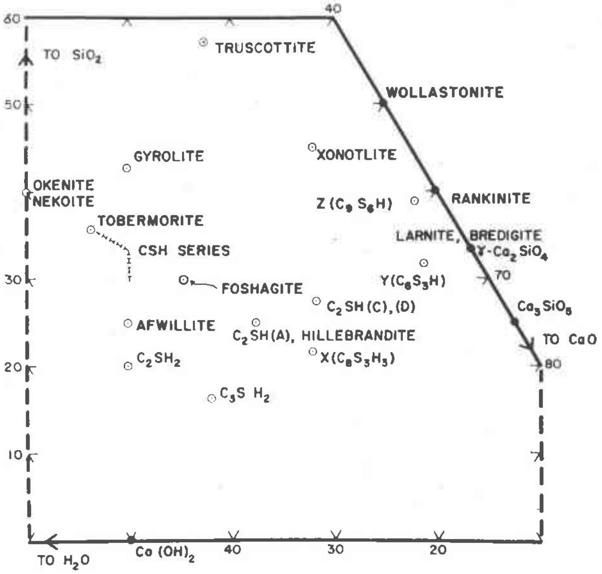

FIG. 1. A portion of the composition diagram for the ternary system CaO-SiO_2-H_2O. Established phases are indicated as well as the new phases X, Y and Z found in the present study; compositions are given in molar ratios CaO:SiO_2:H_2O.

vestigated by hydrothermal techniques, using a variety of starting materials.

EXPERIMENTAL METHODS

Equipment Used

The hydrothermal quenching apparatus used was essentially that described by Roy, Roy and Osborn (1950). Samples were held in gold or platinum envelopes or sealed silver, gold or palladium tubes. In order to avoid hydration during initial heating of the pressure vessel, in a number of cases the pressure was introduced after the bomb had reached the desired temperature. Powder *x*-ray diffraction patterns were obtained on a GE XRD-3 diffractometer and on a Norelco Wide Range diffractometer using filtered Cu radiation. Many samples were examined under the petrographic microscope, and a few infra-red absorption spectra were obtained on a Perkin-Elmer model 21 double beam spectrometer, using on one side a pressed KBr disc "blank" and the other a KBr disc containing about 0.67% of sample.

Starting Materials

The starting materials included natural minerals, mixtures fired to make the anhydrous compounds rankinite, γCa_2SiO_4 and tricalcium silicate; "gels" essentially amorphous to *x*-ray prepared by the method described by R. Roy (1956); and hydrated phases crystallized hydrothermally from gels, anhydrous compounds or mixtures of SiO_2 gel and $Ca(OH)_2$. The products obtained were not analyzed, but reasonable confidence in the compositions was established by checking the homogeneity of the high-temperature phases obtained on firing the samples. During the hydrothermal quenching runs possible change in composition of the material was checked by comparing the product obtained from an ordinary run in a gold envelope with that obtained under similar conditions in a sealed tube which does not permit transfer of any of the material. No substantial difference could be found in the results with most compositions.

RESULTS

New Phases Synthesized

At least three new compounds were formed in the high-CaO portion of the system at elevated temperatures. The probable compositions of the three phases designated X, Y and Z are indicated in Fig. 1. Proposed formulae of these compounds are based on the composition of the starting material and weight loss on ignition of a small sample at 1400° C after drying at 110° C, inasmuch as insufficient material was synthesized to permit accurate analysis. A small amount of CO_2 was no doubt part of the loss under ignition, particularly in X. The new phases are relatively low in H_2O content, and they were found to be stable to remarkably high temperatures, which is consistent with this observation. An additional needle-shaped phase was formed at temperatures around 700° C at high pressures, but insufficient data have been obtained to fully describe this phase and its stability limits at the present time. Refractive indices are: $n_\gamma = 1.612$, $n_\alpha = 1.598$; extinction parallel or very nearly so, +elongation. Principal *x*-ray diffraction lines are: 7.4w, 3.68mw, 3.28s, 2.89vs, 2.58vw, 2.318vw, 2.027mw, 1.622vw.

Optical Properties

X phase ($C_8S_3H_3$) occurs generally as low birefringent crystals with poorly developed crystal faces. Very low birefringent crystal sections have an olivine-like shape with, however, inclined extinction of about 18°, negative elongation. Refractive indices are: $n_\gamma = 1.636$, $n_\alpha = 1.630$; interference figure is probably biaxial positive with a very small 2V. Y phase (C_6S_3H) occurs as moderately low birefringent plates or prisms with $n_\alpha = 1.650$, $n_\beta = 1.661$, $n_\gamma = 1.664$, biaxial negative, 2V smaller than 30°, negative elongation with extinction angle 15°. The symmetry is apparently not higher than monoclinic. The optical properties easily distinguish this phase from β and γ Ca_2SiO_4. Z phase (C_9S_6H) is difficult to distinguish optically from rankinite, having approximately the same index of refraction ($n_\gamma = 1.654$ and $n_\alpha = 1.649$), and the crystals are seldom well enough formed to enable accurate determination of the indices. However, it is easily identified by its *x*-ray diffraction pattern.

X-ray Diffraction Data

X-ray diffraction patterns for the phases X, Y, and Z are given in Table I. These were obtained on a Norelco wide range diffractometer using filtered Cu radiation. The patterns are diagnostic for each of the phases and are easily distinguished from those of the established lime-silica hydrates. Certain reflections of the X-phase are also characteristic of calcite, and the latter phase frequently occurs as impurity in high-CaO products; however, the pattern of X is sufficiently complex to distinguish it from a mixture of calcite and another lime silicate phase. Taylor (personal communication, 1958) has recently synthesized a phase of apparent composition C_5S_2H, the properties of which agree well with those of X. This will be discussed further in a later section. Dent and Taylor in dehydration studies of afwillite have also encountered a poorly crystallized phase similar to Z (Dent, 1957).

Infra-red Spectra

Infra-red absorption spectra obtained for the compounds X, Y, and Z previously dried at 110° C. are given in Fig. 2. The spectrum of Y-phase is distinct from those of β and γCa_2SiO_4 (see Roy, 1958) having two very small absorption bands present in the OH-H_2O region, at 2.81 and 2.91 microns, which is consistent with the minor H_2O content in the proposed formula $3Ca_2SiO_4 \cdot H_2O$. Z-phase showed even smaller absorption maxima at 2.82 and 2.91 microns, in agreement with the proposed formula $3Ca_3Si_2O_7 \cdot H_2O$. The spectra of Z and Y are rather complex at longer wave lengths, and no interpretations are made of these, except that they do demonstrate the unique character of each phase. X-Phase ($8CaO \cdot 3SiO_2 \cdot 3H_2O$), in contrast to Y and Z, showed a greater intensity of absorption at 2.82 and 2.90 microns. Possible absorption due to $CO_3^{=}$ is present at 6.9 microns, but this is probably the spectrum of calcite, which is frequently present as impurity in high-lime mixtures, and which was identified optically in a small quantity in the particular sample used for the spectrum. It cannot be maintained that CO_2 is essential to the formation of X-phase, inasmuch as the compound forms from anhydrous Ca_3SiO_5 (heated to 1400° C.) as well as from gels formed at lower temperatures which would be more likely to contain adsorbed CO_2.

Other Phases Present

Crystals of C_3SH_2 were well-formed needles or laths, the optical properties and *x*-ray diffraction pattern agreeing with those reported by Mc-

TABLE 1. POWDER *X*-RAY DIFFRACTION DATA ON NEW CALCIUM SILICATE HYDRATES*

X($C_8S_3H_3$) No. 940		Y(C_6S_3H) No. 509		Z(C_9S_6H) No. 948		$CaCO_3$** Calcite		$Ca(OH)_2$***	
d(Å)	I/I_0	*d*(Å)	I/I_0	*d*(Å)	I/I_0	*d*(Å)	I/I_0	*d*(Å)	I/I_0
8.45	.25			5.10	.2				
		6.90	.25	4.76	.1			4.90	.74
5.435	.7			4.18	.1				
4.351	.2	4.61	.1	3.970	.2				
4.220	.6			3.758	.1	3.86	.12		
4.020	.2	3.435	.7	3.670	.1				
3.832	.45	3.349	.25	3.559	.4				
3.708	.1	3.293	.2						
3.346	.55	3.258	.25						
3.143	.05	3.209	.05						
3.043	.65	3.067	.5	3.057	.75	3.035	1.00	3.112	.23
2.950	.35	2.986	.4						
2.920	.6	2.890	.25	2.883	1.0				
2.815	.25	2.860	.15	2.840	.3	2.845	.03		
2.781	.45	2.823	.35						
2.716	.6	2.736	.10	2.733	.1				
2.582	.25	2.718	.20						
2.561	.35	2.634	.15	2.673	.75			2.628	1.00
2.526	.3	2.594	.02						
2.498	.25	2.556	.25	2.549	.2				
2.481	.1	2.488	.02	2.481	.2	2.495	.14		
2.372	.1	2.473	.02	2.424	.3			2.447	.03
2.326	.1	2.290	1.0	2.350	.15				
2.144	.1	2.270	.05	2.264	.05	2.285	.18		
2.110	.05	2.243	.02						
2.026	.1	2.135	.05			2.095	.18		
1.914	.55	2.002	.10	1.964	.3				
1.901	.25	1.936	.05	1.902	.15	1.927	.05	1.927	.42
1.875	.05					1.913	.17		
1.855	.05					1.875	.17		
1.829	.15			1.833	.3				
1.811	.55							1.796	.36
1.783	.05								
1.727	.05	1.725	.02	1.749	.2				
1.700	.15	1.716	.25						
1.690	1.0			1.692	.1			1.687	.21
1.665	.25	1.635	.02			1.626	.04	1.634	.01
						1.604	.08		
1.558	.1			1.570	.05				
						1.587	.02	1.557	.03
1.461	.05			1.489	.05	1.525	.05		

* Filtered Cu radiation using Norelco Wide Range Diffractometer; spacings considered accurate to ±0.002 Å at 3.3 Å.

** Calcite data from H. Swanson and R. Fuyat, Standard X-Ray Diffraction Patterns, Natl. Bur. Stand. Circular 539, Vol. II, 52–53 (1953).

*** $Ca(OH)_2$ data from H. Swanson, E. Tatge, *ibid.*, Vol. I, 59 (1953).

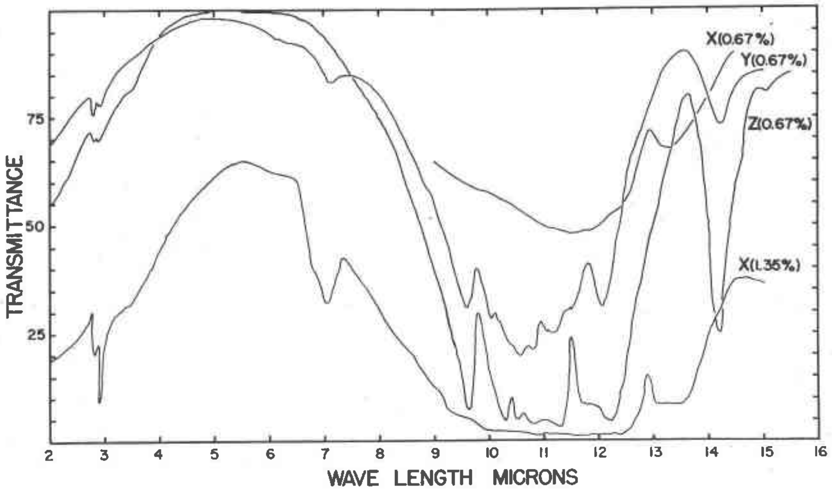

FIG. 2. Infra-red absorption spectra for X($C_8S_3H_3$), Y(C_6S_3H) and Z(C_2S_6H) using KBr method.

Murdie and Flint (1943). *X*-ray patterns of γ and βCa_2SiO_4 are consistent with earlier data (Roy, 1956_a). Rankinite crystallized hydrothermally formed small very low birefringent crystals, with $n_\beta = 1.644$. The *x*-ray diffraction patterns of rankinite formed in the present study, both hydrothermally and "dry" at elevated temperatures differ slightly from previous data (Clark, 1946; Heller and Taylor, 1956), and therefore typical patterns of hydrothermal and "dry" rankinite are given in Table II. The comparison between the two is quite good, with, however, some differences in the intensity pattern of the reflections.

Foshagite, although apparently not a stable phase in the composition range studied ($CaO:SiO_2$ ratios of from 3:1 to 3:2) was formed in trial runs in which excess SiO_2 was added to the 3:2 composition, and also in an occasional run of long duration from 3:2 $CaO:SiO_2$ mixture, in which CaO was believed to be leached out, leaving a CaO-poor mixture. Approximate conditions of formation were 450° C., 15,000–30,000 psi, although no attempts were made to define a region of stability. These observations, however, suggest that the formula proposed by Gard and Taylor (1958) having a $CaO:SiO_2$ ratio of 4:3 is more correct than the previous approximation 5:3 (Eakle, 1935).

Hydrothermal Phase Equilibria

Hydrothermal quenching data used to determine the p-T curves of Fig. 3 are summarized in Table III. In all cases more than one type of

TABLE 2. POWDER *X*-RAY DIFFRACTION DATA ON RANKINITE

Rankinite 1385° 24 hrs.		Rankinite 850°, 20,000 psi 3 days		Rankinite 1385° 24 hrs.		Rankinite 850°, 20,000 psi 3 days	
d(Å)	I/I_0	*d*(Å)	I/I_0	*d*(Å)	I/I_0	*d*(Å)	I/I_0
		6.4	.02	2.281	.1	2.278	.05
		5.62	.1			2.228	.05
5.43	.3	5.44	.2	2.193	.2	2.198	.05
		5.19	.1	2.166	.3	2.167	.2
4.48	.4	4.49	.3	2.134	.1	2.139	.1
4.10	.3	4.09	.15	2.110	.1	2.110	.05
3.84	.4	3.84	.5	2.047	.1	2.039	.05
3.786	.4	3.79	.5	1.998	.1	1.987	.1
		3.58	.15	1.968	.8	1.970	.2
3.382	.2	3.380	.2	1.963	.6	1.964	.1
3.238	.2			1.958	.5	1.958	.05
3.198	.3	3.200	.6	1.922	.8		
3.174	.6	3.177	.7	1.916	.3	1.919 br	.05
3.013	1.0	3.019	1.0			1.886	.05
		2.990	.1	1.864	.1	1.864	.2
2.903	.2	2.906	.6	1.832	.3	1.835	.1
		2.791	.1	1.828	.3	1.828	.05
2.780 br	.3	2.770	.15	1.819	.4	1.820	.2
2.746	.9	2.750	.2	1.800	.05	1.802	.02
2.719	.9	2.718	.8	1.761	.2	1.743	.05
2.714						1.738	.05
2.607	.5	2.609	.1			1.734	.05
		2.594	.3			1.730	.05
2.592		2.580	.3	1.632	.02	1.635	.1
2.578	.5	2.542	.1	1.611	.2	1.611	.05
2.522	.4	2.523 br	.3			1.599	.05
2.508	.1			1.588	.1		
2.366	.1						
2.300	.05						

starting material was used in the hydrothermal runs, to provide a reasonable check on the attainment of equilibrium. For example, for curve IV, when C_3S, $X+Ca(OH)_2$ and crystalline C_3SH_2 all yield the same product it is clear that equilibrium has been attained. It was fairly easy to reverse the equilibria involving C_3SH_2, X, Y, C_2S, and C_3S for curves I, III, and IV (i.e., phases above and below a particular p-T curve could be converted readily to the other assemblage). Rankinite, however, was not readily hydrated, and curve II is based on results from decomposed afwillite and more than one gel. Afwillite was not synthesized sufficiently

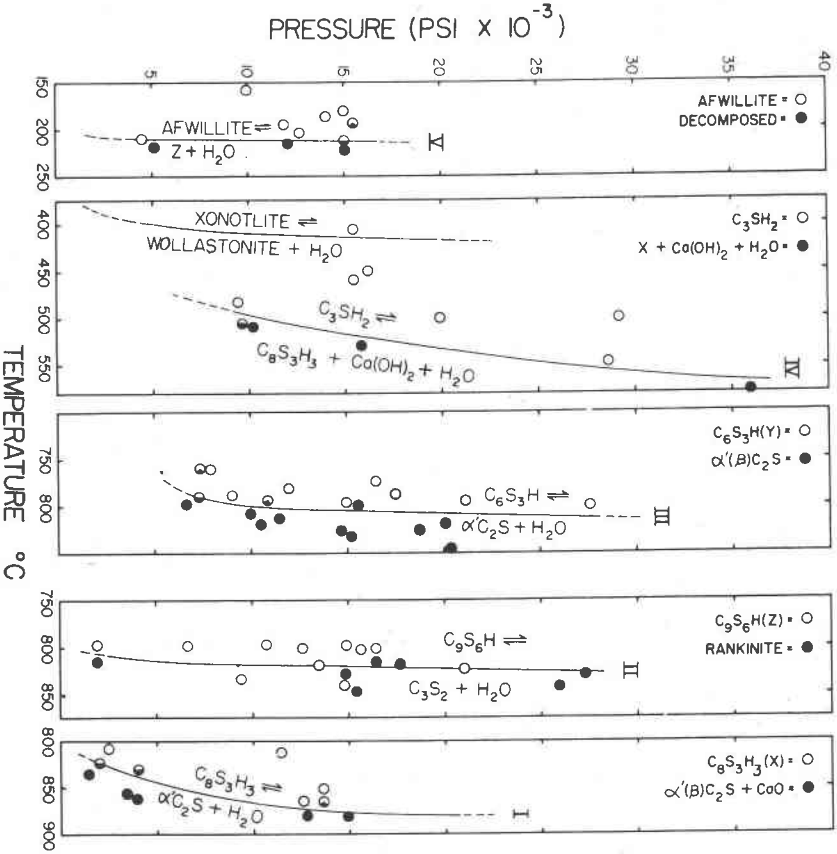

FIG. 3. Pressure-Temperature equilibrium curves for reactions in the system CaO-SiO_2-H_2O. Xonotlite⇌Wollastonite+H_2O is from Buckner and Roy (1955).

free from other phases to enable use as a starting material, so the results for curve V are based on results of the decomposition of two different samples of natural afwillite, which gave closely similar results.

The temperature for the reaction $X = \alpha' Ca_2SiO_4$ (βC_2S on quench) $+ CaO + H_2O$ (curve I) varies from about 820° C. at 2,000 psi to about 875° C. at 15,000 psi. Curve II for $Z =$ rankinite$+H_2O$ does not show a significant variation with pressure, which is not surprising in terms of the low H_2O content of Z, and the optical properties which would suggest not very different densities for Z-phase and rankinite. The best value on the curve seems to be about 820° C. at 15,000 psi. Y-phase is in equilibrium with $\alpha' Ca_2SiO_4 + H_2O$ at 803° C. and 10,000 psi, and 815° C. at 15,000 psi. Attempts made to obtain points at pressures of 30,000 psi or greater

TABLE 3. HYDROTHERMAL QUENCHING DATA FOR THE SYSTEM $CaO\text{-}SiO_2-H_2O$

Composition Mol %		Run No.	Temp. ° C.	Press. psi	Time days	Remarks (Starting Material)	Phases Present
CaO	SiO_2						
						Curve I	
75	25	540	880	15,000	1	CS-15(Xln C_3S)	β C_2S largely
75	25	593	880	12,800	1	CS-15(Xln C_3S)	β C_2S largely
75	25	571	869	13,700	1	CS-15(Xln C_3S)	X phase+β
75	25	568	854	13,700	1	CS-15(Xln C_3S)	X phase largely
75	25	723	761	16,000	1	CS-29(Xln C_3S)	X+l $Ca(OH)_2$
75	25	592	880	12,800	1	CS-19(C_3S gel)	β C_2S 1. CaO
75	25	581	812	11,500	3	CS-19(C_3S gel)	X largely
75	25	541	880	15,000	1	CS-5 (C_3S gel)	β C_2S largely
75	25	572	869	13,700	1	CS-5 (C_3S gel)	X+l β C_2S
75	25	214	807	2,500	1	CS-5 (C_3S gel)	X largely
75	25	227	825	2,000	1	CS-5 (C_3S gel)	β+X+CaO
75	25	222	835	1,500	1	CS-5 (C_3S gel)	β+CaO
75	25	234	832	4,000	1	CS-5 (C_3S gel)	β+X+CaO
75	25	245	857	3,500	1	CS-5 (C_3S gel)	β+l X+CaO
75	25	257	862	4,000	2	CS-5 (C_3S gel)	β+CaO
71	29	594	880	12,800	1	CS-18(C_5S_2 gel)	β C_2S largely
71	29	582	812	11,500	3	CS-18(C_5S_2 gel)	X+β C_2S
						Curve II	
60	40	321	800	2,000	1	gel CS-7	Z phase
60	40	93	815	2,000	5	gel CS-7	Rankinite
60	40	826	799	6,700	1	mixture CS-32	Z
60	40	747	810	16,500	1	mixture CS-32	Z+l Woll
60	40	754	818	16,500	1	mixture CS-32	Rank+l Woll
60	40	1206	799	10,800	1	gel CS-31	Z phase
60	40	937	803	12,700	3	gel CS-31	Z
60	40	934	820	13,600	1	gel CS-31	Z
60	40	1226	833	9,400	1	gel CS-31	Z
60	40	931	834	14,900	1	gel CS-31	Z
60	40	924	845	15,200	3	gel CS-31	Rank
60	40	963	824	21,000	1	gel CS-31	Z
60	40	939	829	27,300	1	gel CS-31	Rank
60	40	943	842	26,000	2	gel CS-31	Rank
60	40	512	800	15,000	8	gel CS-7	Z
60	40	621	803	15,500	1	gel CS-7	Z
60	40	629	820	17,700	1	gel CS-7	Rank
60	40	578	828	14,800	1	gel CS-7	Rank
						Curve III	
67	33	824	760	7,500	1	$Ca(OH)_2$+qtz reacted (CS-33)	Y phase largely
67	33	764	790	7,300	1	$Ca(OH)_2$+qtz reacted (CS-33)	Y largely
67	33	1193	791	9,000	5	CS-17 gel	Y phase
67	33	603	790	17,500	3	CS-17 gel	Y largely
67	33	1209	799	10,800	1	CS-17 gel	Y phase+l β C_2S
67	33	619	803	15,500	1	CS-17 gel	β largely
67	33	1213	805	10,000	1	CS-17 gel	β+l X
67	33	583	812	11,500	3	CS-17 gel	β+l X
67	33	529	685	4,000	13	CS-14 (γ C_2S)	Y largely
67	33	825	760	7,500	1	CS-14 γ C_2S	β C_2S+Y
67	33	763	790	7,300	1	CS-14 γ C_2S	β C_2S+l γ
67	33	828	799	6,700	1	CS-14 γ C_2S	β C_2S
67	33	564	781	12,000	3	CS-14 γ C_2S	Y phase largely
67	33	584	812	11,500	3	CS-14 γ C_2S	Y C_2S+β C_2S
67	33	727	774	16,500	1	CS-14 γ C_2S	Y phase
67	33	638	810	22,500	19	CS-14 γ C_2S	β+l γ?+Y?
67	33	576	828	14,800	1	CS-14(γ C_2S)	β+l γ
67	33	509	800	15,000	8	CS-11(γ C_2S)	Y phase
67	33	496	830	15,000	10	CS-11 (γ C_2S)	β C_2S
67	33	1192	791	9,000	5	1045 (γ C_2S)	Y phase
67	33	1268	799	10,800	1	1045 (γ C_2S)	β C_2S+l Y
67	33	1212	805	10,000	1	1045 (γ C_2S)	β C_2S+l X
67	33	1222	815	10,300	1	1045 (γ C_2S)	β C_2S
67	33	1194	791	9,000	5	865 (Y phase)	Good Y
67	33	955	798	21,200	1	866 (β C_2S)	Y phase
67	33	958	804	27,500	3	866 (β C_2S)	Y phase
67	33	951	815	20,100	1	866 (β C_2S)	β largely

Abbreviations: X = crystalline; $\beta=\beta$ C_2S; Woll = Wollastonite; Rank = rankinite; qtz = quartz; Cc = calcite; l = little; decomp = decomposition.

Where wollastonite was formed it agrees with the pattern of Heller and Taylor (1955) but is undistinguished from para-wollastonite.

TABLE 3 (*Continued*)

Composition Mol %		Run No.	Temp. ° C.	Press. psi	Time days	Remarks (Starting Material)	Phases Present
CaO	SiO_2						
67	33	949	826	18,750	1	866 (β C_2S)	β largely
67	33	946	850	20,400	3	866 (β C_2S)	β C_2S
						Curve IV	
75	25	676	231	12,000	4	C_3SH_2 (No. 666)	C_3SH_2
75	25	702	410	15,500	3	C_3SH_2 (No. 666)	C_3SH_2 largely
75	25	711	454	15,900	3	C_3SH_2 (No. 666)	C_3SH_2 largely
75	25	725	460	15,500	5	C_3SH_2 (No. 666)	$X+C_3SH_2$
75	25	1220	483	9,400	1	C_3SH_2 (No. 666)	$C_3SH_2+X+Ca(OH)_2$
75	25	1197	500	29,200	1	C_3SH_2 (No. 666)	C_3SH_2+l X
75	25	1189	504	20,000	1	C_3SH_2 (No. 666)	C_3SH_2+X+l $Ca(OH)_2$
75	25	1225	507	9,800	1	C_3SH_2 (No. 666)	C_3SH_2+some X+CC+$Ca(OH)_2$
75	25	700	525	15,900	1	C_3SH_2 (No. 666)	X largely+$Ca(OH)_2$
75	25	1186	580	36,000	1	C_3SH_2 (No. 666)	X+l calcite+l $Ca(OH)_2$
75	25	1230	507	10,000	2	C_3SH_2 (No. 666)	X+Cc+$Ca(OH)_2$
75	25	712	454	15,900	3	$X+Ca(OH)_2$(CS-35)	$X+C_3SH_2$+some $Ca(OH)_2$
75	25	1219	483	9,400	1	$X+Ca(OH)_2$(CS-35)	$X+Ca(OH)_2+C_3SH_2$
75	25	744	485	12,700	5	$X+Ca(OH)_2$(CS-35)	$X+Ca(OH)_2$
75	25	1196	500	29,200	1	$X+Ca(OH)_2$(CS-35)	C_3SH_2+X+l $Ca(OH)_2$
75	25	1188	504	20,000	1	$X+Ca(OH)_2$(CS-35)	$X+C_3SH_2+Ca(OH)_2$
75	25	1224	507	9,800	1	$X+Ca(OH)_2$(CS-35)	$X+Ca(OH)_2$
75	25	1229	507	10,000	2	$X+Ca(OH)_2$(CS-35)	$X+Ca(OH)_2$+l Cc
75	25	1185	580	36,000	1	$X+Ca(OH)_2$(CS-35)	$X+Ca(OH)_2$+l Calcite
75	25	666	204	12,400	4	Ca_3SiO_5 (CS-22)	C_3SH_2
75	25	677	297	1,500	1	Ca_3SiO_5 (CS-22)	C_3SH_2
75	25	682	386	6,400	1	Ca_3SiO_5 (CS-22)	C_3SH_2
75	25	703	410	15,500	3	Ca_3SiO_5 (CS-22)	$C_3SH_2+X+Ca(OH)_2$
75	25	724	460	15,500	5	Ca_3SiO_5 (CS-22)	$C_3SH_2+X+Ca(OH)_2$
75	25	743	485	12,700	5	Ca_3SiO_5 (CS-22)	$X+Ca(OH)_2$
75	25	701	525	15,900	1	Ca_3SiO_5 (CS-22)	$X+Ca(OH)_2$
75	25	1218	483	9,400	1	Ca_3SiO_5 (1044)	$X+Ca(OH)_2$
75	25	1195	500	29,200	1	Ca_3SiO_5 (1044)	C_3SH_2+X
75	25	1187	504	20,000	1	Ca_3SiO_5 (1044)	C_3SH_2+X+l $Ca(OH)_2$
75	25	1223	507	9,800	1	Ca_3SiO_5 (1044)	$X+Ca(OH)_2$
75	25	1228	507	10,000	2	Ca_3SiO_5 (1044)	$X+Ca(OH)_2$
75	25	1184	580	36,000	1	Ca_3SiO_5 (1044)	$X+Ca(OH)_2$+l Calcite
						Curve V	
60	40	850	157	10,000	7	Afwillite-Crestmore	Afwillite
60	40	835	188	15,000	8	Afwillite-Crestmore	Afwillite
60	40	818	190	14,200	1	Afwillite-Crestmore	Afwillite
60	40	814	194	15,200	1	Afwillite-sealed tube	Decomp; Z beginning?
60	40	797	218	15,000	5	Afwillite-sealed tube	Partly decomp
60	40	771	291	11,500	1	Afwillite-sealed tube	Z phase largely
60	40	627	200	12,000	1	Afwillite-Megaw	Afwillite
60	40	669	204	12,400	4	Afwillite-Megaw	Afwillite
60	40	647	215	12,200	15	Afwillite-Megaw	Decomp
60	40	656	214	15,000	1	Afwillite-Megaw	Some decomp?
60	40	635	212	12,000	1	Afwillite-Megaw	Some decomp?
60	40	643	211	4,500	1	Afwillite-Megaw	Afwillite
60	40	663	219	5,100	4	Afwillite-Megaw	Decomp

were beyond the practical limit of the apparatus at such high temperatures except for short runs. However, it was doubtful that equilibrium was attained under such conditions, inasmuch as the results thereby obtained were not consistent.

C_3SH_2 was in equilibrium with $X+Ca(OH)_2$ (curve IV) at temperatures ranging from about 505° C. at 10,000 psi to 520° C. at 15,000 psi to 570° C. at 30,000 psi. The reaction was fairly easily reversible, although there was some indication of persistence of C_3SH_2 above the curve in short runs. C_3SH_2 was formed as low as 200° C. in the present study. The curve for the equilibrium xonotlite = wollastonite + H_2O is taken from Buckner and Roy (1955). Curve V was obtained using two samples of afwillite,* one from Scawt Hill and the other from Crestmore. Both samples gave closely comparable decomposition temperatures, about 210° C. at 15,000 psi. The decomposition product just above the curve was difficult to identify, but at about 300° C. or higher the decomposition product compared well with the Z-phase which is formed from gels at temperatures up to 830° C.

DISCUSSION

Stability of X-phase and Variability in Composition

The phase designated X (suggested composition: $8CaO \cdot 3SiO_2 \cdot 3H_2O$) formed throughout a wide range of conditions of temperature and pressure (see Table IV). Since in most of the runs at lower temperatures anhydrous C_3S was used as the starting material, X was formed from these runs (in equilibrium with $Ca(OH)_2$) only above the upper stability limits of C_3SH_2. It is possible that $C_8S_3H_3$ from its own composition would be stable to much lower temperatures.

X is a well crystallized phase, and was mentioned earlier (along with the synthesis of Y and Z) in connection with studies on dicalcium silicate (Roy, $1956_{a,b}$ and 1958.). No difference in the spacings nor the intensity pattern of the reflections was observed at high temperatures where it was in equilibrium with $\alpha' Ca_2SiO_4$ (from $C_{2.2}S$ and $C_{2.5}S$ compositions) or CaO (from C_3S compositions). Therefore, at least in the approximate range 700–850° C. the phase X is considered to be a unique well crystallized material showing no measurable solid solution. Taylor (personal communication, 1958) has recently synthesized an essentially identical phase having a structure analogous to chondrodite, which he calls "calciochondrodite," $2Ca_2SiO_4 \cdot Ca(OH)_2$. If a calcium analogue of chondrodite is stable it is reasonable to expect one or more of the homologues norbergite, humite or clinohumite (see W. H. Taylor and J. West, 1928, 1929, for structures of chondrodite series) to be formed. In the previously mentioned studies a phase resembling X was formed below about 600° C. at low pressures (Roy, $1956_{a,b}$ and 1958) at the expense of γCa_2SiO_4, the olivine structure. (The apparently unrelated phase Y formed alternatively at high pressures.) A comparison of the x-ray diffraction pattern of X with a typical pattern of the phase formed from dicalcium silicate, designated X* is given in Table V. Many of the stronger lines of X are present in X*, but a variation in the intensity pattern of the lines is observed, and several lines are absent, notably the 001 and 002 (of "calcio-chondrodite" based on Taylor's indexing). These absences would strongly suggest that X* is another of the "calcio-chondro-

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* The generosity of Dr. H. Megaw and of Col. C. M. Jenni in contributing the samples from Scawt Hill and Crestmore, is greatefully acknowledged.

TABLE 4. HYDROTHERMAL QUENCHING RUNS DESCRIBING STABILITY OF X PHASE

Run No.	Temp. ° C.	Press. psi	Time days	Phases Present
		Ca_3SiO_5 Composition		
540	880	15,000	1	β C_2S largely
571	869	13,700	1	X+some β
222	835	1,500	1	β C_2S+CaO
214	807	2,500	1	X largely
206	775	2,000	1	X+CaO
724	460	15,500	5	C_3SH_2+X+$Ca(OH)_2$
682	386	6,400	1	C_3SH_2
597	290	1,000	2	X+$Ca(OH)_2$
666	204	12,400	4	C_3SH_2
		2.5(CaO)(SiO_2) Composition		
582	812	11,500	3	X+l β C_2S
586	772	15,500	6	X+some Y
		2.2(CaO)(SiO_2) Composition		
246	857	3,500	1	β C_2S+l CaO
235	832	4,000	1	β C_2S+X
508	800	15,000	8	X+Y
207	775	2,000	1	X+β C_2S
521	630	10,500	8	X+Y
201	665	2,000	3	γ C_2S+X
182	640	20,000	1	X+Y
249	528	2,000	1	X*
514	433	13,500	6	Y+X*?
		2(CaO)(SiO_2) Composition		
325	750	20,000	2	Y
334	744	2,000	1	β C_2S
328	670	2,000	3	γ C_2S+some X*
262	650	3,500	1	γ C_2S+some X*
288	640	20,000	3	Y
159	590	3,500	3	γ C_2S+X*
271	490	2,000	2	X*
300	500	20,000	3	Y
466	475	15,000	7	Y
242	472	1,500	1	X*
515	433	14,200	6	Y
294	420	20,000	1	unknown
277	320	1,000	1	X*
598	290	1,000	2	X*

Abbreviations X=X phase ($C_8S_3H_3$)
X*=poorly crystallized phase similar to X, see Table IV
Y=Y phase (C_6S_3H)
C_2S=Ca_2SiO_4, l=little

Table 5. Comparison of the *X*-Ray Diffraction Data on the Phases X and X*

X* No. 271 formed from Ca_2SiO_4		X formed from C_8S_3		
d(A°)	I/I₀	*d*(A°)	I/I₀	*hkl* (Taylor's)
		8.45	.25	001
		5.435	.7	$200, 20\bar{1}$
4.37	.05	4.351	.2	
		4.220	.6	002
4.06	.1	4.020	.2	$201, 20\bar{2}$
3.829	.3	3.832	.45	111
		3.708	.1	$210, 21\bar{1}$
3.349	.2	3.346	.55	331
		3.143	.05	
3.045	1.0	3.043	.65	$31\bar{1}$
2.950	.1	2.950	.35	310
2.917	.15	2.920	.6	$202, 20\bar{3}$
2.840	.2	2.815	.25	$40\bar{1}$
2.784	.1	2.781	.45	$31\bar{2}$
2.698	.2	2.716	.6	$400, 40\bar{2}$
2.629	.05	2.582	.25	311
2.556	.1	2.561	.35	$11\bar{3}$
2.525	.2	2.526	.3	$211, 21\bar{3}$
		2.498	.25	$41\bar{1}$
2.481	.15	2.481	.1	$120, 12\bar{1}$
		2.372	.1	$401, 40\bar{3}$
		2.326	.1	
		2.144	.1	
		2.110	.05	
1.949	.02	2.026	.1	$402, 40\bar{4}$
1.913	.5	1.914	.55	$222, 22\bar{3}$
1.899	.2	1.875	.05	
		1.855	.05	$420, 42\bar{2}$
		1.829	.15	511
		1.811	.55	$600, 60\bar{3}$
		1.783	.05	
		1.727	.05	
		1.700	.15	
1.689	.2	1.690	1.0	(005)
1.667	.2	1.665	.25	
1.556	.1	1.558	.1	
		1.461	.05	

dite" series. Unexplained are absences of *h*00 spacings, although sufficient *hk*0 spacings are present to suggest the same general type of framework. Furthermore, the line 1.689 is present, though diminished in intensity, which would correspond to the interlayer distance between successive oxygen (or hydroxyl) sheets characteristic of the chondrodite type structures containing Ca.

The poorly crystallized nature of this phase (X*) makes tentative the suggestions outlined. There is the problem of reconciling possible formulae with the composition of the starting material $2CaO \cdot SiO_2$; however, the material, being poorly crystallized might contain amorphous SiO_2. It is an additional problem to determine what is the stable phase under these conditions. The phase Y is apparently stable at higher pressures at least as low as 475° C., and X*, though formed reproducibly, may be only metastable.

Chondrodite in the MgO-SiO_2-H_2O System

The stable hydrothermal formation of a calcium analogue of chondrodite was unexpected, inasmuch as chondrodite had never been encountered in the studies of the system MgO-SiO_2-H_2O (Bowen and Tuttle, 1949) or MgO-Al_2O_3-SiO_2-H_2O (Roy and Roy, 1955). Three alternatives would immediately come to mind to explain failure to achieve synthesis of the chondrodite series: (1) F^- is essential to the *stability* (not only formation) of the structures, (2) chondrodite is stable with a deficiency of H_2O in the region where the assemblage serpentine+brucite is stable with excesss H_2O (under the hydrothermal experimentation conditions), or (3) chondrodite is actually only a metastable phase.

Inasmuch as the previous work (Bowen and Tuttle, 1949; Roy and Roy, 1955) only incidentally provided information on stable assemblages involving forsterite, serpentine and brucite, it was decided to make a few more exploratory runs in this region. Gels of the compositions 2.5 $MgO \cdot SiO_2$ and $3MgO \cdot SiO_2$ and a sample of natural chondrodite from Orange Co., New York* were used as starting materials. Runs were made in the temperature interval immediately below the decomposition of brucite, roughly 430–650° C. at pressures of from 5,000 to 35,000 psi for periods of time varying from 15 minutes to 10 days.

The results obtained were somewhat inconclusive. Although the shorter runs did not bring about decomposition of chondrodite, in most cases the 001 and 002 spacings were diminished or absent, and other changes in the *x*-ray powder pattern took place, especially reinforcement of the 200 line.

No positive evidence for synthesis of chondrodite (or norbergite) from gels was obtained, and in most cases the final product was a mixture of brucite+forsterite. In some of the shorter runs at low pressures weak

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* F. A. Genth collection, No. 415.12, College of Mineral Industries, The Pennsylvania State University.

lines at ca. 7.4 and 3.72 Å were observed which could possibly correspond to 001 and 002 of chondrodite, but more than likely correspond to 001 and 002 of poorly crystallized serpentine formed during the few minutes of heating up to temperature.

Other Observations on Chondrodite Stability

In view of the failure to achieve synthesis of chondrodite and other members of the homologous series in the system MgO-SiO_2-H_2O, the presence of a stable chondrodite structure in the calcium silicate hydrates was unexpected. The high stability temperature of X (875° C at 15,000 psi) was a further surprise inasmuch as $Ca(OH)_2$ decomposes much lower (about 742° C. at 15,000 psi: Majumdar and Roy, 1956). Natural occurrences of the chondrodite series suggest that the usual mode of formation is alteration of olivine, or retrograde metamorphism where the H_2O pressure would be low, usually associated with limestone. The further alteration of the chondrodite to serpentine is observed, probably at lower temperatures and higher water pressures.

The converse seems to be true in the calcium silicate instance, where the lime olivine γCa_2SiO_4 is stable only below about 675° C. at moderately low pressures (Roy. In press.) and is "up-graded" through the formation of the chondrodite phase Ca^{++} is present in six-fold coordination in γCa_2SiO_4, and apparently in calcio-chondrodite and $Ca(OH)_2$, while the more dense forms of Ca_2SiO_4 in which Ca^{++} is present in a higher coordination state with respect to oxygen are stable above 675° C. The combination of the olivine and $Ca(OH)_2$ layers to form the chondrodite structure apparently enhances the stability of the six-coordinated polyhedra, and the combination structure is stable to a higher temperature than either of the components.

The Role of H_2O in the Structures of the Hydrates

The proposed formula for X-phase, $C_8S_3H_3$ suggests a higher H_2O content than that of Taylor (C_5S_2H). The formula $C_8S_3H_3$ is based on total ignition loss, and it is recognized that a small amount of $CaCO_3$ is present, which may well explain the difference. Infra-red absorption spectra, however, show two maxima in the "water-band" region, and a second type of "water" may be present in addition to the hydroxyls of the $Ca(OH)_2$ layer (Fig. 2).

The infra-red absorption spectra of the phases Y and Z, respectively, show diminishing amounts of "H_2O," and similarly have two separate maxima in this region. The poorly crystallized phase resembling Z obtained by Dent from the decomposition of afwillite (Dent, 1957) appears to be anhydrous; however, this is not surprising, in view of the fact that any number of pseudo-phases may be cited, particularly clays, micas, etc., in which the water has been almost totally removed and yet essentially the same *x*-ray pattern persists. The low H_2O content of Z and similarity in the refractive indices to those of rankinite, suggest not too different densities and probably similar coordination of the calcium ions in the two phases; and the formation of Z-phase seems to be a logical step on the way to the formation of rankinite.

Y-phase appears to be unrelated to any of the known hydrates, and thus far has not been formed at low pressures (below about 5,000 psi). Having relatively high refractive indices, it appears to be more closely related to the structures of the higher temperature polymorphs of Ca_2SiO_4, α' or β; it converts readily to the latter on heating "dry" at temperatures of about 800° C. or higher.

It has been generally accepted that the H_2O content of C_3SH_2 is variable, and no attempt was made in the present study to determine the actual composition—the optical properties and *x*-ray diffraction pattern were sufficient to establish the identity of the phase with the phase previously described by Flint, McMurdie and Wells (1938) and others. No positive evidence was obtained for more than one step in the process of breakdown of the C_3SH_2 structure, i.e., the optical and *x*-ray data were consistent up to the temperature of decomposition. A temperature interval over which the three phases C_3SH_2, X and $Ca(OH)_2$ coexist was found, but this may be the result of leaching out of some CaO to change the total composition. A few runs in sealed tubes in which the total composition of the sample cannot change suggest that this is the explanation. Therefore, the maximum temperature at which C_3SH_2 was formed was taken as the upper stability limit.

The hydrothermal decomposition of afwillite similarly failed to reveal more than one step in the process. The optical properties and *x*-ray diffraction pattern remained those characteristic of well crystallized afwillite up to the temperature of the decomposition curve. The fact that hydrothermal decomposition takes place nearly 100° C. lower than dehydration at atmospheric pressure (about 300° C., Parry and Wright, 1925) is not surprising, inasmuch as the hydrothermal decomposition is believed to be an equilibrium reaction. Dent (1957) has pointed out the fact that during dehydration at atmospheric pressure a steady gradual weight loss is observed, and the weight loss curves are based on extent of dehydration during a "reasonable" length of time.

Natural Occurrences

The apparent formation of the three phases X, Y and Z throughout a wide temperature range was surprising inasmuch as none of the three are known to occur naturally. Four possible explanations for their absence in known calcium silicate localities might be proposed:

1. The deposits are formed at high temperatures above about 800° C.
2. The deposits were formed at high or intermediate temperatures in the absence of sufficient H_2O to give rise to hydrates.
3. Reaction was dominated by CO_2 from limestone, and silicate-carbonates were formed.
4. Reaction to form calcium silicates took place at high temperatures, and later low temperature hydrothermal alteration gave rise to comparatively low temperature hydrates such as afwillite, hillebrandite or perhaps foshagite.

A combination of 2, 3 and 4 appears to be the case at Crestmore (Burnham, 1954). The results of the present study, however, may not be strictly applicable where MgO is a component. Monticellite is stable under water pressure of about 15,000 psi as low as 475° C., and merwinite as low as 625° C., though not as low as 475° C. (Roy, 1956a).

Wollastonite is by far the most common of the anhydrous calcium silicates. Although other factors have also to be considered, wollastonite would be expected to be relatively abundant in contrast to hydrate minerals, from the comparatively low decomposition temperature of the $CaSiO_3$-hydrate stable to highest temperatures, xonotlite—decomposing at about 420° C. at 15,000 psi (Buckner and Roy, 1955).

While tobermorite type structures undoubtedly play the dominant role in the binder of portland cement, it would be worthwhile to examine various poorly crystallized cement materials for the presence of X or Z. These phases are apparently formed stably at low pressures—although probably not at ordinary temperatures, but steam cured or autoclaved materials might provide sufficiently high temperatures. The phase Y formed only at moderate or high pressures and would not be expected under similar conditions as X and Z; and cement phases having the ratios $2CaO \cdot SiO_2$ would be more likely to contain a mixture of X and Z.

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