U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1147

Part of Journal of Research of the National Bureau of Standards, Volume 21, November 1938

FORMATION OF HYDRATED CALCIUM SILICATES AT ELEVATED TEMPERATURES AND PRESSURES

By Einar P. Flint, Howard F. McMurdie, and Lansing S. Wells

ABSTRACT

An X-ray investigation of the crystalline hydrated calcium silicates which occur naturally as minerals indicated that the following are distinct compounds: Okenite, $CaO.2SiO_2.2H_2O$; gyrolite, $2CaO.3SiO_2.2H_2O$; crestmoreite, $2CaO.2SiO_2.3H_2O$; xonotlite, $5CaO.5SiO_2.H_2O$; afwillite, $3CaO.2SiO_2.3H_2O$; foshagite, $5CaO.3SiO_2.3H_2O$; and hillebrandite, $2CaO.SiO_2.H_2O$. Riversideite is apparently not a distinct mineral and is probably the same compound as crestmoreite. Crystalline preparations having X-ray patterns identical with those of gyrolite, xonotlite, and foshagite were synthesized by hydrothermal treatment of calcium silicate in the form of the anhydrous crystalline compounds, glass, and amorphous hydrate. Other compounds formed were cristobalite, wollastonite, pseudowollastonite, $4CaO.5SiO_2.5H_2O$, $CaO.SiO_2.H_2O$, $10CaO.5SiO_2.6H_2O$, $2CaO.SiO_2.H_2O$, and $3CaO.SiO_2.2H_2O$. A low-temperature modification of anhydrous tricalcium disilicate, which inverts to the usual form at 1,024° ± 5° C, resulted from the action of water vapor on tricalcium disilicate at 500° C, 380 atmospheres. Gyrolite was obtained at temperatures between 150° and 400° C, $4CaO.5SiO_2.5H_2O$ at 150° to 275°C, $CaO.SiO_2.H_2O$ at 150° C, xonotlite at 175° to 390° C, wollastonite at 400° C and higher, foshagite at 300° to 350° C, $10CaO.5SiO_2.6H_2O$ at 100° to 200° C, and $3CaO.SiO_2.2H_2O$ at 200° to 450° C. Attempts to prepare okenite, crestmoreite, afwillite, and hillebrandite were unsuccessful. Treatment of tricalcium and dicalcium silicates with water at room temperature for several years gave crystalline alteration products which were different from other known hydrated calcium silicates. That derived from dicalcium silicate had a composition approaching $3CaO.2SiO_2.1.5H_2O$. Attempts to isolate and identify the hydrated calcium silicate binding material in commercial sand-lime brick and in laboratory-prepared brick were unsuccessful, but a partial separation of the cementing material was apparently obtained. Applications of the results to the autoclave testing of cements are discussed.

CONTENTS

I. INTRODUCTION

The suggested application to portland cement [1] [1] of the autoclave test for soundness has renewed interest in the products of reactions between cement constituents and water at elevated temperatures and pressures. Among the possible products of such treatment are crystalline hydrated calcium silicates. Such compounds occur in nature as a group of rare but widely distributed minerals commonly found in contact zones of limestone and silicates and are evidently formed by hydrothermal processes. A number of unsuccessful attempts have been made to identify the cementing material of sand-lime brick with some of the naturally occurring calcium hydrosilicate minerals [2].

About a dozen apparently distinct varieties of these minerals are listed by J. W. Mellor [3], but several of these are based on analyses of impure specimens and inadequate optical data. For this reason it was necessary, first of all, to make a study of the natural minerals to ascertain which of these are actually distinct species. Hydrothermal syntheses of some, and determinations of the range of temperatures and pressures over which they are stable, were made. Certain difficulties were encountered. Chief among these was the slow crystallization rate of the hydrated calcium silicates, some of which apparently require months or even years to form at the lower temperatures. Consequently, the ranges of stability of the various phases have been only partially ascertained. Another difficulty lay in the close similarity in crystal habit and optical properties of most of the compounds. Confirmation by means of X-ray patterns was necessary in many cases.

II. X-RAY IDENTIFICATION OF HYDRATED CALCIUM SILICATE MINERALS

As many as possible of the hydrated calcium silicates already identified as distinctive minerals were obtained for further identification by means of X-ray diffraction patterns.[2] All were either from type localities or localities from which specimens described in the literature had been secured. Table 1 gives the name, locality, formula, and literature references accompanying the specimens of which X-ray diffraction patterns were made. Powder X-ray diffraction patterns were made also of the anhydrous calcium silicates: $3CaO.SiO_2$, β-$2CaO.SiO_2$, γ-$2CaO.SiO_2$, $3CaO.2SiO_2$, α-$CaO.SiO_2$ (artificial pseudowollastonite), and wollastonite.

---

[1] Figures in brackets indicate the literature references at the end of this paper.

[2] Practically all of these minerals were obtained from the United States National Museum, through the kindness of W. F. Foshag, Curator of Mineralogy.

TABLE 1.—*Hydrated calcium silicate minerals*

Name	Formula	Locality	Literature reference
Okenite	$CaO.2SiO_2.2H_2O$	Crestmore, Calif.	Eakle, Univ. Calif. Bul. Dept. Geol. **10,** 327 (1917).
Centrallasite	$4CaO.7SiO_2.5H_2O$	Wet Weather Quarry, Crestmore, Calif.	Foshag, Am. Mineral. **9,** 88 (1924).
Truscottite	$4(Ca,Mg)O.7SiO_2.5H_2O$	Benkoelen, Sumatra	Grutlerink, Verh. Geol.-Mignt. Genootschaap, Nederland, Geol. Series **8,** 197 (1925).
Gyrolite	$4CaO.6SiO_2.5(H,Na,K)_2O$	Niakornat, Greenland	Boggild, Medd. am Grönl. **34,** 93 (1908).
Crestmoreite	$2CaO.2SiO_2.3H_2O$	Crestmore, Calif.	Eakle, Univ. Calif. Bul. Dept. Geol. **10,** 327 (1917).
Riversideite	$2CaO.2SiO_2.H_2O$	Crestmore, Calif.	Eakle, Univ. Calif. Bul. Dept. Geol. **10,** 327 (1917).
Xonotlite	$5CaO.5SiO_2.H_2O$	Isle Royale, Mich.	Foshag and Larson, Am. Mineral. **7,** 23 (1922).
Afwillite	$3CaO.2SiO_2.3H_2O$	Dutoitspan Mine, Kimberly, South Africa.	Parry and Wright, Mineralog. Mag. **20,** 277–96 (1925).
Foshagite	$5CaO.3SiO_2.3H_2O$	Crestmore, Calif.	Eakle, Am. Mineral. **10,** 97 (1925).
Hillebrandite	$2CaO.SiO_2.H_2O$	Velardena District, Durango, Mexico.	Wright, Am. J. Sci. **26,** 551 (1908).

The results of this study were as follows: The minerals gyrolite, centrallasite, and truscottite, were found to be very closely related. All of the lines in the pattern of gyrolite were present in the same positions in the pattern of the truscottite sample. The truscottite sample, however, had additional lines, the more intense of which corresponded to the more intense lines of quartz. The sample of centrallasite also possessed lines common to gyrolite and truscottite as well as the more intense lines of quartz. The recorded optical properties of these minerals are also very similar; all three have the same maximum index of refraction, 1.549; all are optically negative; and gyrolite is unaxial, while centrallasite and truscottite are reported to have very small optic angles. All three of the samples studied contained perceptible amounts of isotropic material with low index of refraction occurring as microscopically thin crusts on the platy crystals or as fine laminae between the plates.

Of the hydrated monocalcium silicates, xonotlite has a pattern which is characteristic and distinctive. Some confusion has existed regarding the two minerals riversideite and crestmoreite, which possess crystallographic properties identical within experimental accuracy. Their discoverer, A. S. Eakle [4], distinguished between them by the greater water content of crestmoreite and presented a typical analysis of this mineral which corresponded to the ratios $1.09CaO:1.00SiO_2:1.27H_2O$, after correcting for the P_2O_5, SO_3, and CO_2 present. Similarly, the analysis given for riversideite conformed to the ratios $1.01CaO:1.00SiO_2:0.62H_2O$. The analyses showed that both minerals had the same impurities in comparable amounts.

In order to determine the significance of these reported differences in water content, some experiments were made on a sample of crestmoreite obtained from the United States National Museum. The loss on ignition to a temperature of 1,100° C was 13.09 percent. After heating the crestmoreite at 110° C for 3 hours, the loss on ignition (H_2O+CO_2) was reduced to 9.80 percent, which is only slightly higher than the water content of 8.11 percent reported for riversideite. The indices and appearance of the crystals were unchanged and the distinctive X-ray pattern of the original mineral was not altered, which indicated that the water was not constitutional.

Another characteristic of riversideite, according to Eakle, was its occurrence in narrow seams in mounds of vesuvianite, whereas crestmoreite was associated with calcite. However, a sample labelled "riversideite," from Ward's Natural Science Establishment, in which the hydrated calcium silicate appeared as narrow veins in lumps of vesuvianite, was found by its X-ray pattern to be identical with crestmoreite from the United States National Museum. Thus, crestmoreite may occur associated with the same mineral as was reported for riversideite.

A sample labelled "riversideite" from the United States National Museum showed complete identity of pattern with foshagite from the Museum. The identical X-ray diffraction pattern of a preparation obtained by treating $5CaO\cdot 3SiO_2$ glass with water (as will be described later) indicates that both are foshagite.

Because no sample of riversideite could be obtained which was distinct from other minerals, and, in view of the fact that none of its reported properties are characteristic it is believed that riversideite does not exist as an independent compound.

A sample labelled "foshagite" from the Wet Weather Quarry, Crestmore, Calif., obtained from Ward's Natural Science Establishment, was found to be made up of two minerals. One gave an X-ray pattern identical with that of foshagite; the other was identical with that of hillebrandite from the Velardena Mines, Mexico—both samples were obtained from the United States National Museum. This may account for the fact that Vigfusson [5] found the X-ray patterns of foshagite and hillebrandite identical and concluded that they were the same mineral. The remaining minerals, okenite, afwillite, and hillebrandite, gave characteristic and distinctive X-ray patterns.

A sample of an unknown hydrated calcium silicate mineral obtained from the United States National Museum proved to be distinctive in X-ray pattern and optical properties. Analysis gave the following composition: 35.57 percent of CaO, 0.30 percent of MgO, 1.19 percent of R_2O_3, 42.7 percent of SiO_2, 19.76-percent ignition loss; total 99.61 percent. The amount of sample available was insufficient for a CO_2 determination, but petrographic examination indicated that the amount of carbonate present was probably less than 5 percent. Assuming the ignition loss to represent the water content, the analysis conforms to $0.89CaO:1.00SiO_2:1.54H_2O$, which does not correspond very closely to any simple CaO/SiO_2 ratio. The sample consisted of aggregates of fibrous crystals having parallel extinction, positive elongation, and indices of refraction[3] $\alpha=1.540 \pm 0.003$, $\gamma=1.548 \pm 0.003$. Some finely divided material as well as glassy isotropic impurity was present.

III. HYDROTHERMAL SYNTHESIS OF HYDRATED CALCIUM SILICATES

1. MATERIALS

The starting materials were precipitated hydrated calcium silicate, calcium silicate glass, and the crystalline anhydrous calcium silicates.

A previous investigation [6] had shown that solutions containing

---

[3] In this paper α and γ are used to indicate the minimum and maximum refractive indices, respectively, although, in some cases, it is not certain that the crystals are biaxial.

0.5 g SiO_2/l and about 0.05 g CaO/l can be prepared by boiling purified silica gel with dilute lime solution for several days. By adding saturated limewater to such a solution in varying proportions, hydrated calcium silicate precipitates were prepared having CaO/SiO_2 molar ratios ranging from 0.1 to 1.5. The precipitates were washed with alcohol and ether, dried in a desiccator over calcium chloride, and analyzed to determine their CaO/SiO_2 molar ratios. These preparations are designated in the tables by the letters "aq" to indicate their indefinite water content.

The calcium silicate glasses were prepared by quenching charges of the proper compositions wrapped in platinum foil from temperatures above the liquidus. Small amounts of boric oxide were added to some of these charges to bring the temperature of complete melting within the range of the furnace.

The anhydrous calcium silicates were laboratory preparations of high purity.

2. APPARATUS AND EXPERIMENTAL PROCEDURE

Four bombs were used in this investigation, three of which were constructed according to designs of the Geophysical Laboratory [7]. Two of these bombs are of stainless steel and of 40-ml capacity, and one is of tool steel and of 18-ml capacity. These bombs were heated in insulated Nichrome-wire furnaces having heating zones twice as long as the bombs. By means of modified bimetallic regulators, each furnace could be maintained at temperatures between 150° and 600° C within ±5°C for long periods of time.

Temperatures were measured by means of Chromel-Alumel thermocouples in conjunction with a portable potentiometer. The thermocouples were inserted in wells drilled in the bombs.

The calcium silicate starting materials were inclosed in platinum capsules of 3-ml capacity and placed with water in the bombs in such a way that the solid was in contact with the liquid at temperatures below the critical point of water. Sufficient water was always used so that the liquid phase was present up to the critical point (374° C, 218 atm.). The pressures below 374° C are therefore those of saturated steam in contact with liquid water; those above 374° C were read from the the curves of van Nieuwenburg and Blumendal [8], knowing the mass of water inserted and the volume of the bomb.

After completion of the heating period, the bomb was removed from its furnace and cooled by immersion in water; the product was then removed, washed with alcohol and ether, and dried in a desiccator over a mixture of calcium chloride and soda-lime or Dehydrite. Petrographic examinations, and, in some cases, chemical analyses were made on the products. X-ray diffraction patterns were taken of most of the preparations for comparison with those of the natural minerals.

The fourth bomb is of 2-liter capacity, is made of tool steel, and was used up to 225° C. As figure 1 shows, it was so designed that the liquid and solid phases could be quickly separated without opening the bomb. In use the bomb was first inverted and the materials were placed in the compartment designed as upper chamber in the figure. The bomb in this position was placed in a heating oven equipped with a fan. On completion of the heating period, the bomb

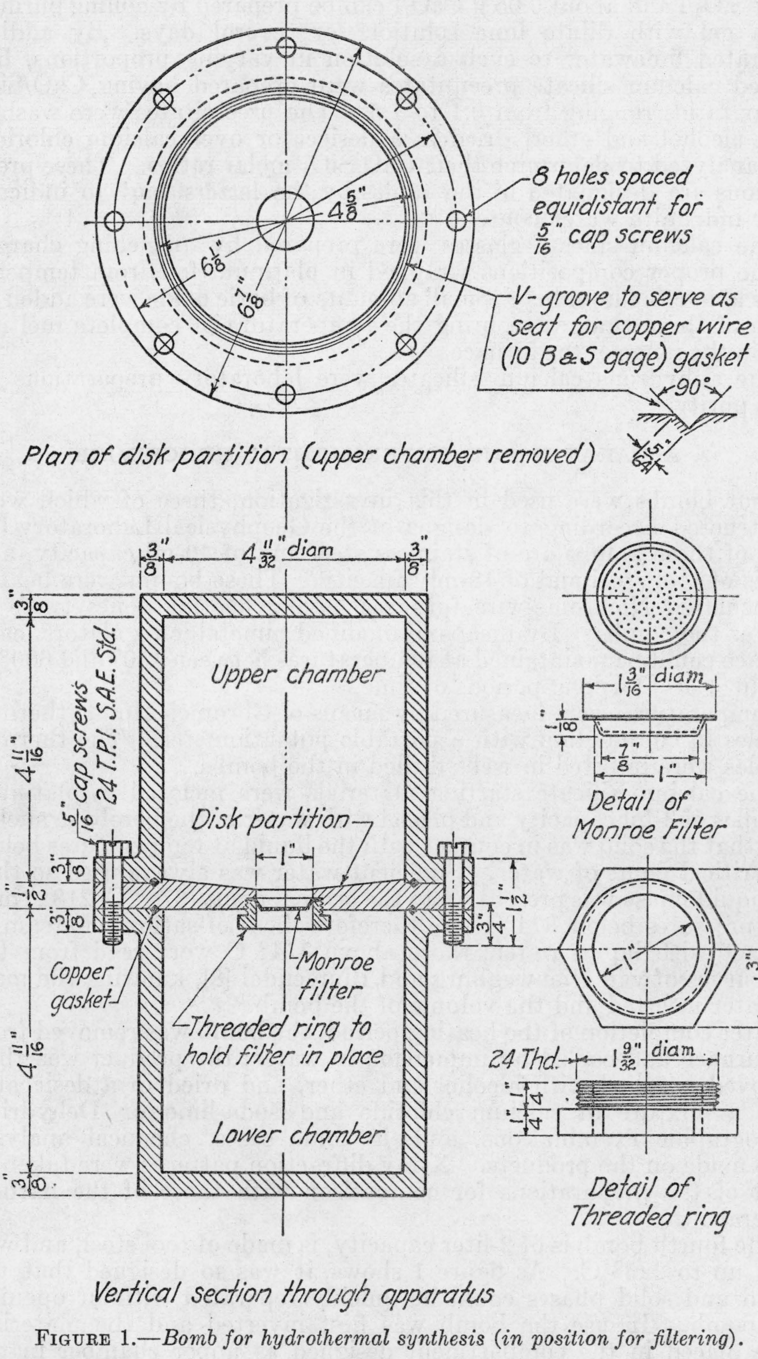

FIGURE 1.—*Bomb for hydrothermal synthesis (in position for filtering).*

was turned over and the lower chamber (fig. 1) placed in cold water. Condensation of steam in this chilled compartment forced the liquid through a Munroe platinum filter in the middle disk.

3. PRELIMINARY EXPERIMENTS

At a given temperature and pressure the composition of the product will depend not only on the composition of the starting material, but also on the relative solubilities of lime and silica in the liquid. The CaO/SiO_2 ratio of the product may be either raised or lowered, depending upon whether lime or silica has the greater concentration in the solution formed.

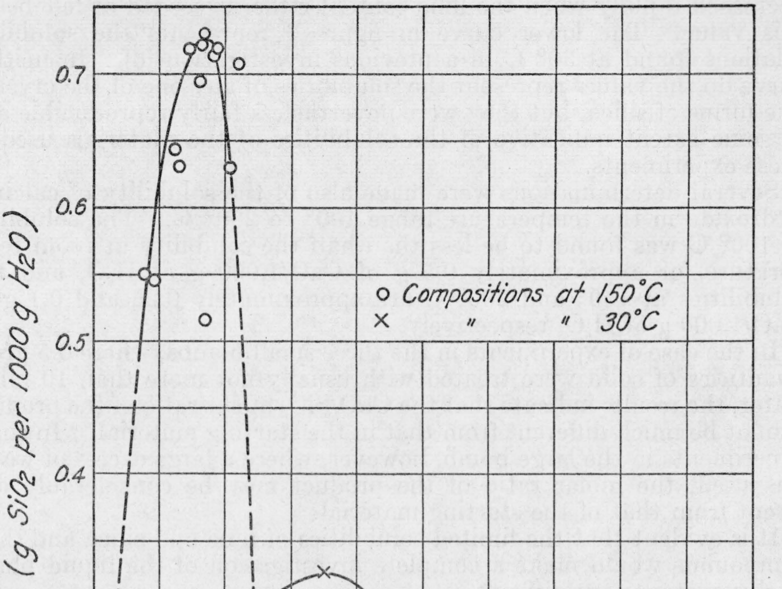

FIGURE 2.—*Solubilities of silica in lime solutions at 30° and 150° C.*

To obtain some information on this factor, a number of determinations were made of the solubility of amorphous silica in solutions of calcium hydroxide at 150° C. Silica gel in amounts between 1 and

10 g was treated with 700 ml of lime solution of various concentrations in the large bomb for 5 days with occasional shaking. The resulting solutions, which remained clear for a short time after cooling, were analyzed for lime and silica, and the results are shown in figure 2. The maximum silica concentration was 0.73 g/1,000 g of H_2O at 0.033 g of CaO/1,000 g of H_2O, and the silica content of the solutions decreased rapidly when the lime content either exceeded or fell below this value. The lower curve in figure 2 represents the solubility relations found at 30° C in a previous investigation [6]. In neither curve do the values represent the solubilities of any one of the crystalline forms of silica, but they were nevertheless fairly reproducible and to some extent indicative of the solubilities of the materials used in these experiments.

Several determinations were made also of the solubility of calcium hydroxide in the temperature range 100° to 200° C. The solubility at 100° C was found to be less than half the solubility at room temperature, or approximately 0.5 g of CaO/1,000 g of H_2O, and the solubilities at 150° and 200° C are approximately 0.25 and 0.1 g of CaO/1,000 g of H_2O, respectively.

In the case of experiments in the three small bombs, where 0.5-gram quantities of solid were treated with usually not more than 10 ml of water, the results indicate that the CaO/SiO_2 molar ratio of the product cannot be much different from that in the starting material. In some experiments in the large bomb, however, where a large excess of water was used, the molar ratio of the product may be considerably different from that of the starting material.

It is evident that the limited solubilities of lime and silica and their compounds would make a complete investigation of the liquid phase in this system very difficult.

4. HYDROTHERMAL TREATMENT OF CALCIUM SILICATES OF VARYING MOLAR RATIOS OF LIME TO SILICA

The effect of hydrothermal treatment on calcium silicates of CaO/SiO_2 molar ratios varying from 0.1 to 4.0 will be described in the following sections. For convenience, the various compositions are divided into groups of the same CaO/SiO_2 ratio or having a limited range of molar ratios. The lengths of time required for complete crystallization to occur varied with the different molar ratios and the periods listed are somewhat arbitrary. In general, however, the times of heating represent those necessary to form a well-crystallized sample as determined by preliminary experiments.

(a) MOLAR RATIO CaO/SiO_2 VARYING FROM 1:10 TO 1:2

The least basic of the known calcium hydrosilicates is the mineral okenite, $CaO.2SiO_2.2H_2O$. The results of treating calcium silicates having the molar ratio of okenite, as well as those of lower molar ratios are described in table 2.

TABLE 2.—*Results of experiments on compositions varying in molar ratio* CaO/SiO_2 *from 1:10 to 1:2*

Experiment number	Starting material	Temperature	Pressure	Time	Product
		°C	atm	Days	
1	$0.1CaO:SiO_2$:aq [1]	390	261	14	Cristobalite+xonotlite.
2	$.2CaO:SiO_2$:aq	450	420	12	Cristobalite+?
3	$.3CaO:SiO_2$:aq	200	15	50	$4CaO.5SiO_2.5H_2O$+?
4	$.5CaO:SiO_2$ glass [2]	150	5	58	Cristobalite+glass.
5	do	225	25	21	Gyrolite+glass.
6	do	300	85	21	Do.
7	do	400	290	7	Do.
8	do	450	300	13	Pseudowollastonite+?

[1] "Aq" here and in following tables designates the indefinite water content of the amorphous calcium silicate precipitates.

[2] Contained 3 percent of B_2O_3.

The crystallization of cristobalite and psuedowollastonite at temperatures far removed from those at which they crystallize from anhydrous melts is of some interest. The cristobalite crystals were very small but good X-ray patterns were obtained. Other investigators have obtained cristobalite by hydrothermal treatment at corresponding temperatures, but usually from neutral or acidic solutions [9]. Xonotlite, $5CaO.5SiO_2.H_2O$, which crystallized with cristobalite in experiment 1, occurred in fairly large, well-formed crystals. Later experiments indicated that xonotlite crystallizes comparatively rapidly at 390° C, which may account for its formation here in preference to less basic hydrosilicates.

In experiment 3 the formation of the compound $4CaO.5SiO_2.5H_2O$, the synthesis of which will be discussed in a later section, cannot be accounted for. The formation of okenite or of gyrolite was more to be expected under these conditions.

The pseudowollastonite obtained in experiment 8 crystallized in aggregates of fibrous needles of parallel extinction and negative elongation. The X-ray pattern was identical with that of α-$CaO.SiO_2$.

The product in experiments 5, 6, and 7 gave the X-ray pattern of gyrolite. In the best crystallized of these preparations, No. 6, the product had the appearance of aggregates of parallel fibers. The ignition loss of this preparation, however, was only 4.8 percent as compared with a theoretical water content for $4CaO.6SiO_2 \cdot 4H_2O$ of 10.97 percent, or for $4CaO.7SiO_2.5H_2O$ of 12.26 percent, which indicated that conversion was incomplete.

Attempts to obtain the mineral okenite were unsuccessful. A product which the authors suggested might be okenite was synthesized by Schlaepfer and Niggli [10] by treatment of mixtures of SiO_2, CaO, Al_2O_3, and KOH with water at 470° C. They reported similarities in appearance and mean index to the natural mineral. These criteria would seem to be insufficient in view of the fact that some of the other hydrated calcium silicates have almost the same index and crystal habit.

(b) MOLAR RATIO CaO/SiO_2 VARYING FROM 4:7 TO 2:3

The CaO/SiO_2 molar ratio 0.59 corresponds to the reported ratio of the minerals centrallasite and truscottite, and the ratio 0.66 corresponds to that of the mineral gyrolite. Results of treatment of such compositions are given in table 3.

TABLE 3.—*Results of experiments on compositions varying in molar ratio* CaO/SiO_2 *from 4:7 to 2:3*

Experiment number	Starting material [1]	Temperature	Pressure	Time	Product
		°C	atm	Days	
9	$0.59CaO:SiO_2$:aq	150	5	42	Gyrolite.
10	do	225	25	28	Do.
11	do	250	39	35	Gyrolite+xonotlite.
12	do	300	85	14	Gyrolite.
13	$0.59CaO:SiO_2$ glass	300	85	37	Do.
14	do	350	163	6	Do.
15	do	450	300	6	Pseudowollastonite+?.
16	$0.66CaO:SiO_2$:aq	250	39	40	Gyrolite.
17	$0.66CaO:SiO_2$ glass	300	85	35	Do.
18	do	500	380	14	Pseudowollastonite+?.

[1] The glasses contained no B_2O_3.

The gyrolite crystals occurred as bundles of parallel fibers with positive elongation, parallel extinction, uniaxial negative, and indices of refraction $\epsilon=1.536$, $\omega=1.548$. A photomicrograph of the preparation from experiment 16 is shown in figure 3. Figure 4 shows preparation 11, which in some portions contained large broom-shaped aggregates of xonotlite surrounded by gyrolite.

A chemical analysis of preparation 10, initial molar ratio 0.59, gave the composition: 34.18 percent of CaO, 55.96 percent of SiO_2, 9.86 percent of H_2O, corresponding to the ratios: $1.96CaO:3.00SiO_2:1.76H_2O$. An analysis of the best preparation, No. 16, initial molar ratio 0.66, gave the composition: 33.58 percent of CaO, 0.36 percent of R_2O_3,[4] 54.02 percent of SiO_2, 11.40 percent of H_2O; corresponding to the ratios: $2.00CaO:3.00SiO_2:2.11H_2O$. These analyses justify assigning to gyrolite the formula $2CaO.3SiO_2.2H_2O$. The fact that the CaO/SiO_2 molar ratio of 0.59 was unstable and increased to 0.65 in experiment 10, while a ratio of 0.66 remained unchanged in experiment 16, indicates that 0.66 is the stable ratio. In conjunction with the X-ray data, this evidence confirms the belief that centrallasite and truscottite are not distinct minerals but are rather impure forms of gyrolite.

The synthesis of gyrolite was claimed by E. Baur [11] from a mixture of SiO_2, Al_2O_3, KOH, and CaO treated with water at 450° C. The optical properties which he reported for his product were, however, not those of gyrolite. No other report on the synthesis of gyrolite was found in the literature.

(c) MOLAR RATIO CaO/SiO_2, 4:5

The results of these experiments are listed in table 4.

TABLE 4.—*Results of experiments on compositions varying in molar ratio* CaO/SiO_2, 4:5

Experiment number	Starting material	Temperature	Pressure	Time	Product
		°C	atm	Days	
19	$0.80CaO:SiO_2$:aq	150	5	42	$4CaO.5SiO_2.5H_2O$.
20	do	225	25	14	Do.
21	do	250	39	7	Do.
22	$0.76CaO:SiO_2$:aq	275	59	21	Do.
23	$0.80CaO:SiO_2$:aq	300	85	14	Xonotlite.
24	do	350	163	10	Do.
25	do	500	380	7	Wollastonite.

---

[4] The small percentages of R_2O_3 in the products of hydrothermal synthesis reported here and elsewhere in this paper are largely Fe_2O_3 as a contamination from the iron of the bomb.

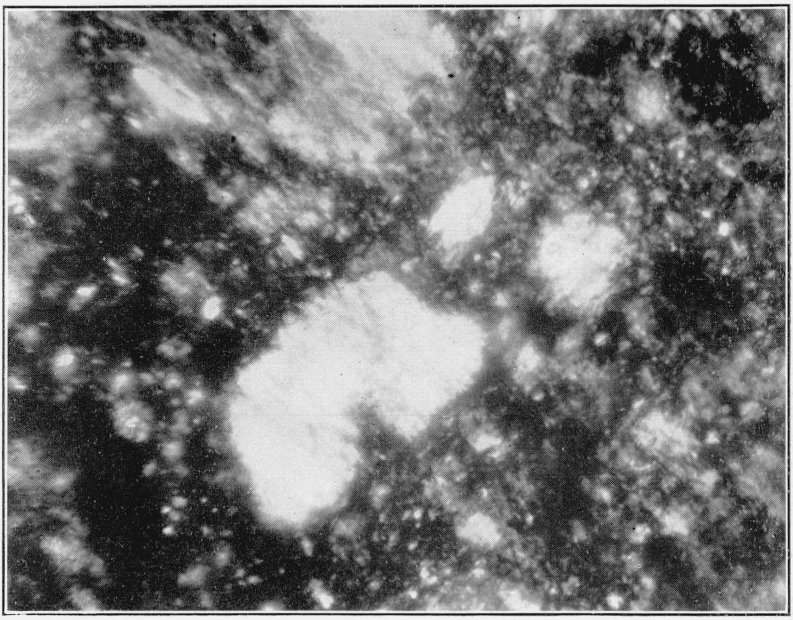

Figure 3.—*Synthetic gyrolite.*

Crossed nicols, magnification ×180

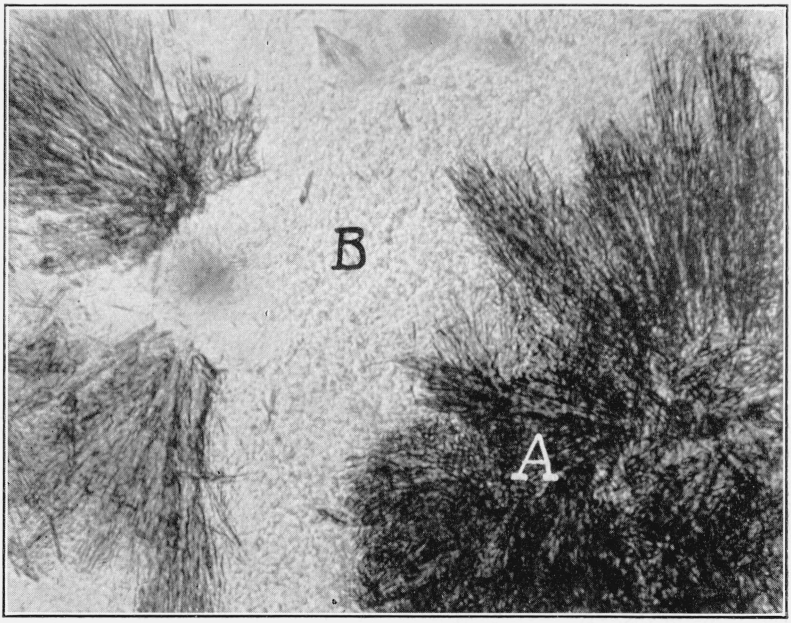

Figure 4.—*Synthetic (A) xonotlite + (B) gyrolite.*

Magnification ×180.

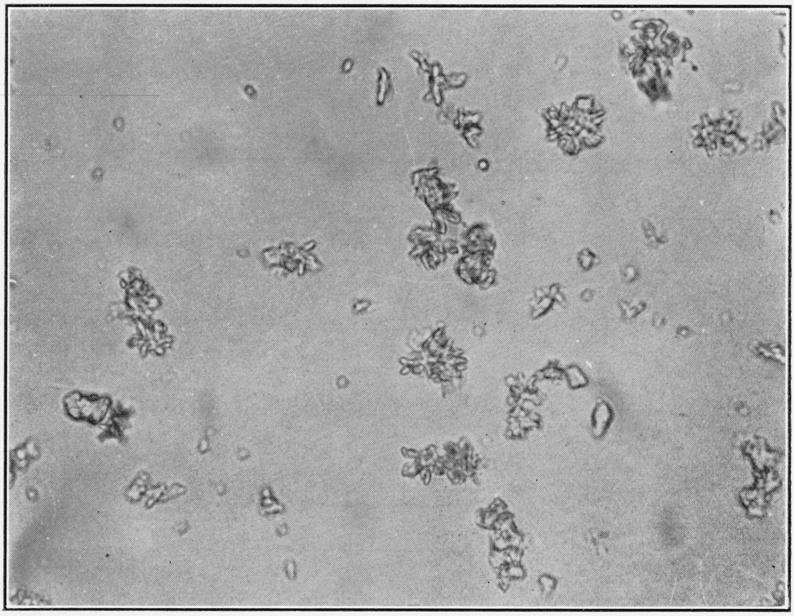

FIGURE 5.—*Synthetic* $CaO.SiO_2.H_2O$.

Magnification ×900.

FIGURE 6.—*Synthetic xonotlite.*

Magnification ×180.

The product of experiments 19, 20, and 21 consisted of very small needles of moderate birefringence and mean refractive index 1.54, positive elongation and parallel extinction. The X-ray pattern of this phase is distinctive. Analysis of preparations 19 and 21 gave the following results:

Components	Preparation 19	Preparation 21
	Percent	*Percent*
CaO	36.86	38.96
R_2O_3	0.37	
SiO_2	47.84	48.71
H_2O	14.44	11.84
Total	99.51	99.51

corresponding to the ratios $4.13CaO:5.00SiO_2:5.03H_2O$ in the case of preparation 19 and to $4.00CaO:5.00SiO_2:4.15H_2O$ for preparation 21. The ignition loss of preparation 20 was 13.97 percent, corresponding to $4CaO:5SiO_2:4.7H_2O$. The formula of this compound is therefore tentatively placed at $4CaO.5SiO_2.5H_2O$.

The mineral most similar to this preparation is tobermorite discovered by M. F. Heddle [12], who assigned to it the formula $3(4CaO.5SiO_2.H_2O).10H_2O$, or $4CaO.5SiO_2.4\frac{1}{3}/H_2O$. P. Groth [13] suggested the formula $4CaO.5SiO_2.4H_2O$. Unfortunately, Heddle was unable to determine the crystalline form of the mineral and lists none of its optical properties, so no further comparison with the synthetic product is possible.

(d) MOLAR RATIO CaO/SiO_2, 1:1

The hydrated monocalcium silicate minerals are crestmoreite, $2CaO.2SiO_2.3H_2O$; and xonotlite, $5CaO.5SiO_2.H_2O$. Experiments on starting materials of this ratio are listed in table 5.

Experiments 26 and 40 involved pseudowollastonite, which underwent no transformation in 6 weeks at 150° C, but it was 50 percent transformed to wollastonite in 3 weeks at 500° C, 480 atmospheres.

TABLE 5.—*Results of experiments on* $1CaO:1SiO_2$ *compositions*

Experiment number	Starting material	Temperature	Pressure	Time	Product
		°C	*atm*	*Days*	
26	Pseudowollastonite	150	5	42	Unchanged.
27	$0.95CaO:SiO_2$:aq	150	5	42	Amorphous.
28	$1.04CaO:SiO_2$:aq	150	5	60	$CaO.SiO_2.H_2O$.
29	do	175	9	79	Xonotlite.
30	do	200	15	73	Do.
31	$1.0CaO:SiO_2$ glass [1]	250	39	10	Do.
32	$1.04CaO:SiO_2$:aq	320	109	7	Do.
33	do	370	207	4	Do.
34	do	380	225	4	Do.
35	do	390	225	4	Do.
36	Xonotlite	390	169	7	Do.
37	do	390	72	4	Do.
38	$1.04CaO:SiO_2$:aq	400	290	5	Wollastonite.
39	do	450	300	5	Do.
40	Pseudowollastonite	500	480	21	50 percent of wollastonite+50 percent of pseudowollastonite.

[1] Contained no B_2O_3.

Amorphous monocalcium silicate hydrate treated with water at 150° C for 6 weeks remained amorphous, but a sample treated for 60 days at the same temperature (experiment 28) crystallized to a single phase of the following composition: 41.97 percent of CaO, 43.97 percent of SiO_2, 14.47 percent of H_2O corresponding to the ratios: $1.02CaO{:}1.00SiO_2{:}1.10H_2O$, or a monohydrate of monocalcium silicate. The preparation was rather finely divided, but under the oil-immersion objective it appeared to be composed of thick needle- and lath-shaped crystals with parallel extinction, negative elongation, mean index 1.603. The X-ray pattern was distinctive and different from that of crestmoreite. A photomicrograph of these crystals is shown in figure 5.

Monocalcium silicate hydrate treated with water between 175 and 390° C for a sufficient time crystallized completely to a product having the optical properties and X-ray pattern of xonotlite, $5CaO.5SiO_2.H_2O$. A typical analysis is that of the preparation from experiment 33 which was: 46.15 percent of CaO, 50.10 percent of SiO_2, 3.35 percent of H_2O, corresponding to the ratios: $0.99CaO{:}1.00SiO_2{:}0.22H_2O$. A photomicrograph of these crystals is shown in figure 6. They are fibrous needles of parallel extinction, positive elongation, having indices of refraction: $\alpha=1.583\pm0.003$, $\gamma=1.594\pm0.003$.

Crystallization of xonotlite occurred most rapidly between 320° and 390° C, in which range it was complete in 4 to 7 days.

Experiments 37 and 38 fix the upper temperature limit at which xonotlite is stable at 395° ±10° C. Xonotlite remained the stable phase at 390° C, on reduction of the pressure from 225 to 72 atmospheres. Above this temperature complete crystallization to large well-formed laths of wollastonite occurred in heating periods of 5 days. A photomicrograph of these crystals is shown in figure 7.

Nieuwenburg and Blumendal [14] reported having obtained wollastonite by steaming a lime-silica mixture out of contact with the liquid for 2 days at 365° C. Their experiment was repeated by steaming monocalcium silicate hydrate out of contact with the liquid at 365° C for 3 days. The product was xonotlite.

Nagai [15] and Kohler [16] reported having synthesized xonotlite, but neither of these authors gives any confirmatory optical or X-ray data.

(c) MOLAR RATIO CaO/SiO_2, 3:2

The mineral afwillite, $3CaO.2SiO_2.3H_2O$, possesses the CaO/SiO_2 molar ratio used in experiments 41 to 49, inclusive, table 6.

TABLE 6.—*Results of experiments on* $3CaO{:}2SiO_2$ *compositions*

Experiment number	Starting material	Temperature	Pressure	Time	Product
		°C	*atm*	*Days*	
41	α-$3CaO.2SiO_2$	150	5	42	>50 percent unaltered.
42	$1.53CaO{:}SiO_2{:}aq$	150	5	70	$CaO.SiO_2.H_2O+$?
43	do	200	15	73	Do.
44	α-$3CaO.2SiO_2$ (prep. 41)	250	39	10	?
45	$1.44CaO{:}SiO_2{:}aq$	250	39	14	Xonotlite+?
46	$1.42CaO{:}SiO_2{:}aq$	300	85	14	Do.
47	$1.45CaO{:}SiO_2{:}aq$	350	163	14	Do.
48	$1.53CaO{:}SiO_2{:}aq$	400	270	5	Do.
49	α-$3CaO.2SiO_2$	500	380	14	β.$3CaO.2SiO_2$.

FIGURE 7.—*Synthetic wollastonite.*

Magnification ×180.

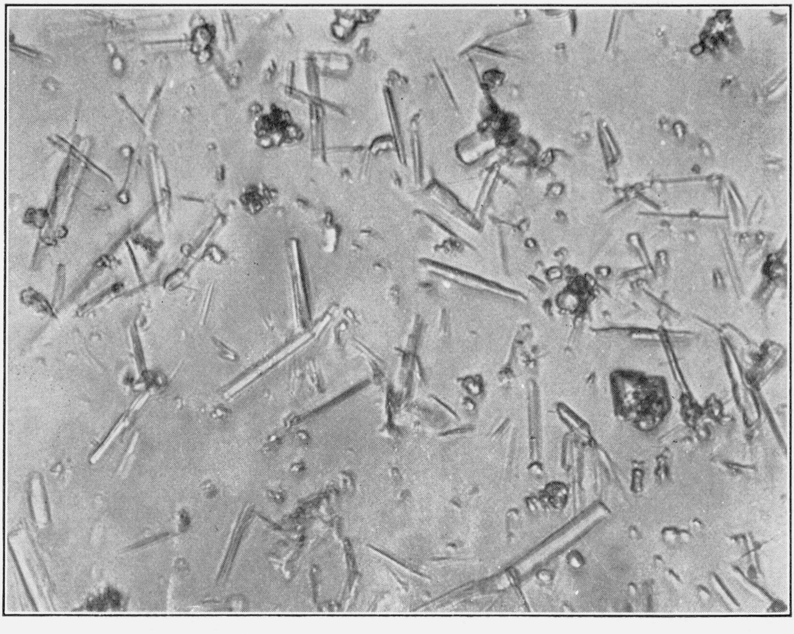

FIGURE 8.—*β-tricalcium disilicate.*

Magnification ×900.

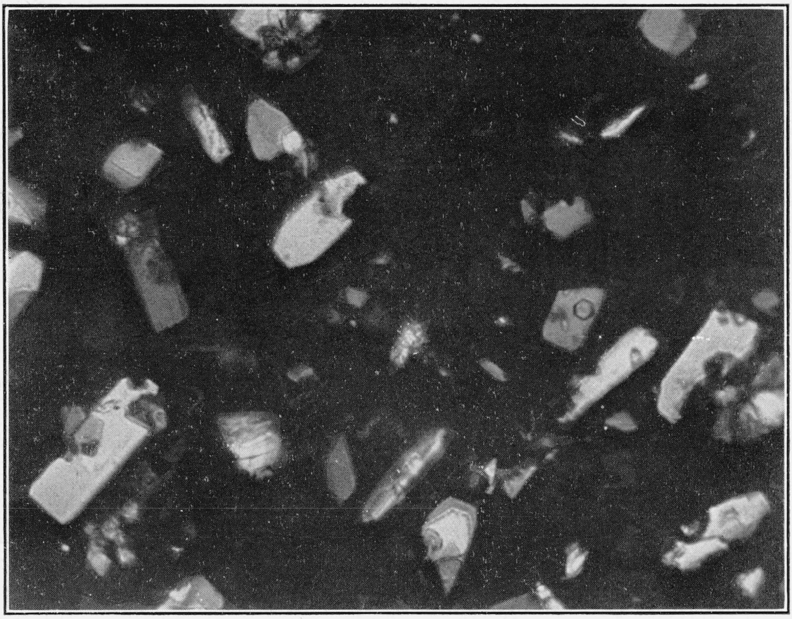

FIGURE 9.—*Synthetic* $10CaO.5SiO_2.6H_2O$.

Crossed nicols, magnification ×400.

In experiment 41 more than 50 percent of the anhydrous tricalcium disilicate, treated with water at 150° C for 6 weeks, remained unaltered. The alteration product consisted of irregular masses of low-birefringent material of refractive index 1.57, and was not identified. This material kept an additional 10 days at 250° C (experiment 44) was largely altered to low-birefringent aggregates of mean refractive index, 1.62+. The X-ray pattern was different from that of afwillite and could not be identified.

Treatment of anhydrous tricalcium disilicate with water at 500° C, 380 atmospheres, for 2 weeks (experiment 49) resulted in 90-percent conversion to a new phase. Inasmuch as the tricalcium disilicate contained a few percent of impurities (mostly dicalcium silicate) there were also present some alteration products of the impurities, including some dicalcium silicate hydrates, the hydrothermal formation of which will be described subsequently. The new phase consisted of small needle- and lath-shaped crystals of parallel extinction and positive elongation. The indices of refraction are: $\alpha=1.608 \pm 0.003$, $\gamma=1.615 \pm 0.003$. A photomicrograph of these crystals is shown in figure 8.

Determinations of ignition loss showed the new compound to be anhydrous. Its X-ray pattern proved to be different from that of ordinary tricalcium disilicate or any of the other anhydrous calcium silicates. Ignition for a few minutes over a Méker burner converted it back to the usual form of tricalcium disilicate.

The evidence indicated that the new phase was a low-temperature form of tricalcium disilicate. This was confirmed by experiments using the quenching method. A sample held overnight at 1,020° C gave an unchanged X-ray pattern, while a sample held at 1,027° C overnight gave the pattern of ordinary tricalcium disilicate. The inversion of the low-temperature form of tricalcium disilicate to the high-temperature form is therefore placed at 1,024°C ±5° C.

Attempts to prepare the mineral afwillite were unsuccessful. Amorphous hydrates having the CaO/SiO_2 molar ratio of this compound when heated at temperatures of 150° and 200° C in the presence of water crystallized largely to $CaO.SiO_2.H_2O$, and at temperatures ranging from 250° to 400° C crystallized largely to xonotlite. The secondary phases could not be distinguished petrographically or by the X-ray patterns. Raising the CaO/SiO_2 molar ratio has the effect of making both $CaO.SiO_2.H_2O$ and xonotlite stable at higher temperatures than was the case with the preparations of pure hydrated monocalcium silicate.

(f) MOLAR RATIO CaO/SiO_2, 5:3

The compositions treated in the experiments reported in table 7 corresponded in lime-silica ratio to the mineral foshagite, $5CaO.3SiO_2.3H_2O$.

TABLE 7.—*Results of experiments on* $5CaO:3SiO_2$ *compositions*

Experiment number	Starting material	Temperature	Pressure	Time	Product
		°C	*atm*	*Days*	
50	1.67$CaO:SiO_2$ glass [1]	200	15	73	?
51	do	300	85	53	Foshagite+glass.
52	do	350	163	17	Foshagite+glass.

[1] Contained 7 percent of B_2O_3.

The product of experiment 50 had the same X-ray pattern as that of the product obtained by treating anhydrous dicalcium silicate and dicalcium silicate glass with water at relatively low temperatures, and will be discussed in the next section.

The product of experiments 51 and 52 was a low-birefringent material without definite crystalline form and of mean index of refraction 1.595, which checks well with the mean index of foshagite. The X-ray patterns showed complete correspondence with the X-ray pattern of foshagite obtained from the United States National Museum. Conversion of the glass to the hydrate was not complete even in experiment 51, as the product gave an ignition loss of only 5.7 percent, compared with a theoretical loss for foshagite of 10.5 percent.

A sample of amorphous hydrate of CaO/SiO_2 molar ratio 1.68 steamed at 300° C out of contact with water gave a product having the X-ray pattern of $CaO.SiO_2.H_2O$. The manner of combination of the excess lime could not be determined.

(g) MOLAR RATIO CaO/SiO_2, 2:1

Results of experiments on compositions having a dicalcium silicate molar ratio, to which the mineral hillebrandite, $2CaO.SiO_2.H_2O$, corresponds, are listed in table 8.

TABLE 8.—*Results of experiments on* $2CaO{:}1SiO_2$ *compositions*

Experiment number	Starting material	Temperature	Pressure	Time	Product
		°C	*atm*		
53	β-$2CaO.SiO_2$	25	1	10 years	?
54	do	100	1	9 days	$10CaO.5SiO_2.6H_2O+\beta$-$2CaO.SiO_2$.
55	γ-$2CaO.SiO_2$	150	5	4 days	$10CaO.5SiO_2.6H_2O+\gamma$-$2CaO.SiO_2$.
56	β-$2CaO.SiO_2$	150	5	1 day	Scarce $10CaO.5SiO_2.6H_2O$ $+\beta$-$2CaO.SiO_2$.
57	do	150	5	7 days	Pure $10CaO.5SiO_2.6H_2O$.
58	$2CaO{:}SiO_2$ gel	150	5	10 days	95% of $10CaO.5SiO_2.6H_2O$.
59	$2CaO{:}SiO_2$ glass (12% of B_2O^3)	150	5	23 days	Same as preparation 53.
60	90% of γ-$2CaO.SiO_2+$ 10% of natural hillebrandite.	150	5	14 days	$10CaO.5SiO_2.6H_2O+$natural hillebrandite.
61	Preparation 53	175	9	41 days	Same product as preparation 53.
62	β-$2CaO.SiO_2$	200	15	3 days	$10CaO.5SiO_2.6H_2O$.
63	$2CaO{:}SiO_2$ gel	225	25	44 days	$2CaO.SiO_2.H_2O$.
64	$3CaO{:}2SiO_2{:}aq+CaO$	225	25	47 days	$CaO.SiO_2.H_2O+$?.
65	β-$2CaO.SiO_2$	250	39	15 days	$2CaO.SiO_2$ aq.
66	$10CaO.5SiO_2.6H_2O$	250	39	14 days	$10CaO.5SiO_2.6H_2O$.
67	90% of γ-$2CaO.SiO_2+$ 10% of natural hillebrandite.	250	39	14 days	Natural hillebrandite$+2CaO.SiO_2$aq.
68	$3CaO{:}2SiO_2{:}aq+CaO$	300	85	7 days	$CaO.SiO_2.H_2O+$?.
69	do	350	163	8 days	$CaO.SiO_2.H_2O+3CaO.SiO_2.2H_2O$.
70	$10CaO.5SiO_2.6H_2O$	450	400	7 days	$2CaO.SiO_2.2/3H_2O$.

Five g of β-dicalcium silicate treated with 500 ml of water for 10 years at room temperature (experiment 53) and shaken at intervals gave a product having a distinctive X-ray pattern and possessing a composition corresponding to the ratios $1.8CaO{:}1.0SiO_2{:}2.1H_2O$. It contained about 5 percent of calcite with the bulk of the material consisting of weakly birefringent masses without definite crystalline form. In order to effect further crystallization this material was heated in the presence of water for 6 weeks at a temperature of 175° C (experiment 61). It was then completely crystallized to very fine needles of low birefringence and mean index of refraction 1.60. A chemical analysis gave the composition: 52.94 percent of CaO, 0.78 percent of R_2O_3, 36.50 percent of SiO_2, 9.69 percent of H_2O, which corresponds to the molar ratios: $1.55CaO:1.00SiO_2:0.88H_2O$. Allowing for the calcite which the sample contained, this analysis agrees fairly well with the formula $3CaO.2SiO_2.1.5H_2O$. The pattern is not like that of afwillite. The same X-ray pattern was given by dicalcium silicate glass (containing 12 percent of B_2O_3) treated with water at 150° C for 3 weeks (experiment 59) and also by $5CaO.3SiO_2$ glass (containing 7 percent of B_2O_3) at 200° C for 10 weeks (experiment 50, table 7).

Treating dicalcium silicate with water between 100° and 200° C usually produces an orthorhombic hydrate of dicalcium silicate. This compound is identical with crystals found by Thorvaldson and Shelton [17] in steam-cured portland cement and prepared in a pure state by Vigfusson, Bates, and Thorvaldson [18]. Reference to the preparation of the same compound from mixtures of lime, silica, and water and from tricalcium silicate and water has also been made by Flint and Wells [6]. The crystals are extremely thin (rarely more than 3 microns in thickness), lath-like plates often occurring as simple rectangular parallelopipeds but not infrequently with domatic faces bevelling the prismatic forms. The measured indices of refraction agree with those fixed by previous investigators: $\alpha=1.614\pm0.002$, $\beta=1.620\pm0.002$, $\gamma=1.633\pm0.002$. The crystals are biaxial positive. There is a perfect cleavage normal to the elongation. A photomicrograph is shown in figure 9.

Analysis of a typical preparation gave the composition: 56.64 percent of CaO, 0.46 percent of R_2O_3, 31.14 percent of SiO_2, and 11.34 percent of H_2O, corresponding to the ratios: $1.96CaO:1.00SiO_2:1.19H_2O$. Prolonged heating in an oven maintained at a temperature of 110° C reduced the water content to 10.90 percent, which corresponds to a H_2O/SiO_2 molar ratio of 1.17. Analysis of several other preparations also gave water contents corresponding closely to $1.2H_2O:1.0SiO_2$. The average of three analyses of this compound presented by Vigfusson, Bates, and Thorvaldson [18] likewise gave a H_2O/SiO_2 molar ratio of 1.24. It, therefore, appears probable that the water in excess of 1 mole is constitutional, and accordingly, the formula $10CaO.5SiO_2.6H_2O$ is suggested for the compound.

As shown in table 8, $10CaO.5SiO_2.6H_2O$ resulted from treatment with water of β- and γ-dicalcium silicates and $2CaO:1SiO_2$ mixtures of calcium oxide and silica gel. At 100° C (experiment 54), 9 days' boiling of 1 g of β-dicalcium silicate with 25 ml of water under a reflux gave about 30-percent conversion to $10CaO.5SiO_2.6H_2O$. Well-formed crystals of $10CaO.5SiO_2.6H_2O$ were also obtained by treatment of portland cement clinkers with water at 100° and 175° C. A photomicrograph of the product obtained at 175° C is given in figure 10.

Attempts to prepare hillebrandite by treating mixtures of natural hillebrandite and dicalcium silicate with water at 150° and 200° C (experiments 60 and 67) were unsuccessful. The results obtained by Kohler [16], who reported having prepared hillebrandite by heating a mixture of β-dicalcium silicate and water at temperatures ranging from 200° to 290° C, could not be duplicated. The synthesis of hillebrandite from mixtures of CaO and amorphous SiO_2 in the presence of $CaCl_2$ heated with water at 470° C has been claimed by Schlaepfer and Niggli [10].

Treatment of $10CaO.5SiO_2.6H_2O$ at 250° C for 2 weeks (experiment 66) produced no change; treatment at 450° C, 400 atmospheres, for 1 week gave a product of unchanged crystal form but having the indices of refraction: $\alpha=1.642$, $\gamma=1.672$, which are about 0.03 higher than the corresponding indices of $10CaO.5SiO_2.6H_2O$. This material gave a distinctive X-ray pattern and its composition corresponded to the formula, $6CaO.3SiO_2.2H_2O$.

In experiment 65, β-dicalcium silicate heated in a bomb with water at 250° C crystallized to a granular product having a mean index of refraction of 1.64. The X-ray pattern was similar in spacing and intensity of lines to that of a finely crystalline monohydrate of dicalcium silicate obtained by Keevil and Thorvaldson [19]. Treatment of a $2CaO:1SiO_2$ mixture of CaO and silica gel at 225° C (experiment 63) gave complete crystallization to the other monohydrated dicalcium silicate described by Thorvaldson and coworkers [18, 19]. This occurs in very small needles of low birefringence and mean index 1.60. Analysis gave a composition corresponding to the ratios $2.0CaO:1.0SiO_2:1.1H_2O$.

In experiments 64, 68, and 69 amorphous hydrated calcium silicate of CaO/SiO_2 molar ratio 3:2 was mixed with sufficient CaO to give a ratio of 2:1 and in the presence of water heated at temperatures of 225°, 300°, and 350° C. The principal product in all three cases was $CaO.SiO_2.H_2O$. The secondary product was not identified except in experiment 69, where the optical properties and X-ray pattern showed it to be a hydrate of tricalcium silicate.

(h) MOLAR RATIO CaO/SiO_2, 3:1

The results of these experiments are shown in table 9.

In experiment 71, 1 g of tricalcium silicate treated with 500 ml of water for 9 years at room temperature was completely converted to a hydrated material of composition $1.3CaO:1.0SiO_2:1.7H_2O$. Petrographic examination showed less than 5 percent of calcite with the bulk of the material appearing as rounded grains of low birefringence having refractive indices ranging from 1.52 to 1.53. The X-ray pattern of this material was different from that of calcite or any of the other hydrous or anhydrous calcium silicates thus far investigated.

TABLE 9.—*Results of experiments on $3CaO:SiO_2$ compositions*

Experiment number	Starting material	Temperature	Pressure	Time	Product
		°C	atm		
71	$3CaO.SiO_2$	25	1	9 years	?
72	do	100	1	14 days	$10CaO.5SiO_2.6H_2O+Ca(OH)_2$.
73	do	150	5	5 days	Do.
74	do	200	15	35 days	$3CaO.SiO_2.2H_2O+10CaO.5SiO_2.6H_2O+Ca(OH)_2$.
75	do	250	39	12 days	$3CaO.SiO_2.2H_2O$.
76	β-$2CaO.SiO_2+CaO$	250	39	10 days	$2CaO.SiO_2$ hydrate$+Ca(OH)_2$.
77	$3CaO:2SiO_2:aq+3CaO$	275	59	16 days	$3CaO.SiO_2.2H_2O$.
78	$3CaO.SiO_2$	350	163	8 days	Do.
79	do	450	397	6 days	Do.

Tricalcium silicate treated with water at 100° C under a reflux condenser (experiment 72) and in the bomb at 150° C (experiment 73)

Figure 10.—*Lath-like orthorhombic plates of synthetic* $10CaO.5SiO_2.6H_2O$ *and hexagonal plates of* $Ca(OH)_2$ *obtained by treatment of portland cement clinker with water at 175° C.*

FIGURE 11.—*Synthetic* $3CaO.SiO_2.2H_2O$.

Magnification ×900.

was converted to $10CaO.5SiO_2.6H_2O$ and calcium hydroxide. At 250° C (experiment 75) direct hydration occurred without liberation of calcium hydroxide. The product consisted of broad fibrous crystals of positive elongation and parallel extinction. The indices of refraction were: $\alpha=1.590 \pm 0.003$, $\gamma=1.602 \pm 0.003$. Analysis of the preparation from experiment 75 gave the composition: 65.42 percent of CaO, 23.45 percent of SiO_2, 11.53 percent of H_2O, corresponding to the ratios: $2.98CaO:1.00SiO_2:1.63H_2O$. At 200° C (experiment 74) the product was primarily this compound with smaller amounts of $10CaO.5SiO_2.6H_2O$ and $Ca(OH)_2$ also present.

For experiment 77 the starting material was a mixture of amorphous hydrate of CaO/SiO_2 molar ratio 3:2 mixed with sufficient CaO to give a ratio of 3:1. After 16 days in the bomb at 275° C this preparation crystallized completely to large broom-shaped clusters of fibrous needles having the composition: 63.07 percent of CaO, 0.50 percent of R_2O_3, 22.38 percent of SiO_2, 13.56 percent of H_2O, corresponding to the ratios: $3.02CaO:1.00SiO_2:2.02H_2O$. A photomicrograph of this material is shown in figure 11. The X-ray pattern and optical properties were the same as those of the product from direct hydration of anhydrous tricalcium silicate. This preparation and that of experiment 75 gave negative tests for free lime by alcohol-glycerol extraction and by White's method.

This compound is identical with the product obtained by Keevil and Thorvaldson [19] by steaming tricalcium silicate between 110° and 375° C. By their procedure, however, only very finely crystalline material resulted.

Dehydration experiments proved the hydrated tricalcium silicate to be a very stable compound. A preparation heated in an oven for 16 hours at 215° C gave a loss in weight of only 0.2 percent. At 500° C for 16 hours the loss was 2.6 percent and at 700° C for 16 hours, 10.3 percent. Ignition for 5 minutes at 1,200° C gave complete conversion of the sample to β-dicalcium silicate and calcium oxide. Attempts to dehydrate the compound to tricalcium silicate were unsuccessful. Loss of water and liberation of free lime appear to take place concurrently.

In experiment 76 an attempt was made to prepare the hydrated tricalcium silicate from a $3CaO:1SiO_2$ mixture of $\beta\text{-}2CaO.SiO_2$ and CaO treated with water at 250° C. The product consisted of calcium hydroxide and the granular dicalcium silicate hydrate obtained by Keevil and Thorvaldson [19] and also identified in experiment 65, table 8 of this paper.

(i) MOLAR RATIO CaO/SiO_2, 4:1

Several experiments which were made to determine whether any hydrates richer in lime than $3CaO.SiO_2.2H_2O$ exist are recorded in table 10.

TABLE 10.—*Results of experiments on $4CaO:1SiO_2$ compositions*

Experiment number	Starting material	Temperature	Pressure	Time	Product
		°C	*atm*	*Days*	
79	$\beta\text{-}2CaO.SiO_2+2CaO$	250	39	7	$2CaO.SiO_2\,aq+Ca(OH)_2$
80	$3CaO.SiO_2+CaO$	250	39	12	$3CaO.SiO_2.2H_2O$.
81	$1.4CaO:SiO_2:aq+2.6CaO$	400	397	7	$3CaO.SiO_2.2H_2O+Ca(OH)_2$.
82	$1.3CaO:SiO_2:aq+2.7CaO$	450	400	6	$3CaO.SiO_2.2H_2O+Ca(OH)_2$.

The results indicate that dicalcium and tricalcium silicates form the same hydrates as they did in the absence of excess lime. The dicalcium silicate hydrate formed in experiment 79 occurred in small irregular plates having refractive indices ranging from 1.62 to 1.64. It was the same product as was obtained in experiment 76, table 9, and experiment 65, table 8 of this paper.

5. CEMENTITIOUS MATERIAL IN SAND-LIME BRICK

Some experiments similar to those of Grime and Bessey [2] were made in an attempt to isolate the hydrated calcium silicate in a commercial sand-lime brick of good quality. Half of the brick was crushed in a porcelain mortar with as little grinding as possible. Of this material the sample passing a No. 40 sieve and retained on a No. 70 sieve after brief shaking was used. It contained 4.4 percent of soluble silica determined according to the usual procedure. The material was screened on a No. 200 sieve for ½ hour and that passing was examined under the microscope. It appeared to consist almost wholly of calcite and was discarded. Screening was then continued another half hour. It was hoped by this method that the cementing material surrounding the sand grains might be rubbed off and concentrated. That this apparently occurred was shown by an increase in soluble silica to 16.2 percent in the material passing the No. 200 sieve. A number of pennies were then added to the material on the No. 200 sieve to assist the rubbing action, and the screening was continued for an hour. The material passing then showed a soluble silica content of 20.2 percent. However, in the X-ray patterns of both samples only the lines of calcite and quartz appeared.

It was thought that evidence of the presence of a crystalline hydrated calcium silicate might be obtained using a laboratory-prepared brick. For this purpose a mixture of 10 percent of hydrated lime and 90 percent of graded Ottawa sand (containing 0.13 percent of soluble silica) was molded into a bar in a hand press. The bar was then treated in contact with water at 175° C for 20 hours. After crushing the brick, the whole sample was found to contain 2.6 percent of soluble silica. This sample was rubbed with the fingers on a No. 20 sieve and the material passing in each case was rubbed successively on the No. 48, 100, and 200 sieves. The material passing the No. 200 sieve contained 16.8 percent of soluble silica. In the X-ray pattern the strongest lines were those of calcium hydroxide together with the lines of quartz.

Another bar was treated in the bomb at 175° C for 15 days. After a separation similar to that just described the material passing a No. 200 sieve was extracted for 75 hours with boiling ethylene glycol in an extractor of the type used in rubber analysis. The residue contained no free calcium hydroxide. Its X-ray pattern showed the lines of quartz with a few additional lines of moderate intensity which did not coincide with any of the lines of quartz, calcite, or calcium hydroxide. It was not possible, however, to assign these additional lines with certainty to any of the known hydrated calcium silicates.

IV. DISCUSSION

In the manufacture of sand-lime brick a wetted mixture of about 10 percent of hydrated lime and 90 percent of sand is pressed into forms, the resulting blocks removed, and steamed in an autoclave at 150° to 200° C (5 to 15 atm) for 8 to 12 hours. The nature of the cementing material formed by this treatment has never been established, but it is presumed to be a hydrated calcium silicate. X-ray and optical data [2] indicate that it may be amorphous. Some inferences regarding its potential crystalline composition may, however, be made from the results of this paper.

Lime usually constitutes only about 10 percent of the sand-lime brick mix, but its proportion to surface silica available for reaction will evidently be much higher owing to the relative coarseness of the sand particles. Thus, it is probable that the cementing material of the brick will be much richer in lime than the mix as a whole. Such a condition might permit the crystallization of compounds as highly basic as $10CaO.5SiO_2.6H_2O$. This compound appears to be by far the most easily formed of the hydrated calcium silicates at the temperatures employed in sand-lime brick manufacture. However, if the lime available for reaction with surface silica is insufficient to form this compound the potential crystallization of a less basic compound such as gyrolite might be favored.

Although the experiments with sand-lime brick failed to establish the identity of the cementing material in sand-lime brick, the greatly increased soluble silica content of the finer fractions of the crushed brick appears to indicate the formation of potentially crystalline compounds. That these combinations could not be identified by their X-ray patterns is not surprising in view of the fact that the various syntheses described in this paper all required much longer periods of time than those employed in sand-lime brick manufacture. The appearance of additional lines in the X-ray pattern of the sand-lime brick treated for a longer period is promising, and it is hoped that further work may reveal their source.

The crystalline materials obtained by reaction of water on β-dicalcium silicate and tricalcium silicate at room temperature are noteworthy with reference to end products in the setting of portland cement. There is a possibility that the product derived from dicalcium silicate, and which had a composition approximating $3CaO.2SiO_2.1.5H_2O$ on complete crystallization, may occur in set portland cement. This product could not be identified with any of the known calcium hydrosilicate minerals.

The poorly crystallized material which resulted from treatment of tricalcium silicate with water at room temperature had a CaO/SiO_2 molar ratio of only 1.3 owing to the extensive hydrolysis which had taken place in the presence of a large excess of water. Therefore, it probably would not form in the setting of portland cement when less water is used but might occur in hydrated puzzolanic cement where the proportion of silica to lime is higher. Unfortunately, the pattern of this material also could not be identified.

As has been pointed out by Thorvaldson and coworkers [17, 18, 19], the compounds designated in this paper as $10CaO.5SiO_2.6H_2O$ and $3CaO.SiO_2.2H_2O$ are probable products of the autoclave treatment of portland cements. Under such conditions it has also been shown by Mather and Thorvaldson [20] that tricalcium aluminate will hydrate to $3CaO.Al_2O_3.6H_2O$ and tetracalcium aluminoferrite to $3CaO.Al_2O_3.6H_2O$ and $CaO.Fe_2O_3$ hydrate, which, in turn, will slowly decompose to $Ca(OH)_2$ and hematite. Thus it would appear possible to hydrate cement partially in the autoclave without the liberation of appreciable free lime. This is actually the case. A group of four high-tricalcium silicate cements all having ignition losses and free-lime contents of less than 1 percent was steamed in the autoclave at 200° C (15 atm) overnight. The ignition loss in each case was increased to 5 to 6 percent. The free-lime content of one cement remained the same, another showed a slight decrease, and the two remaining, an increase of a few tenths of a percent.

With regard to the 215° C autoclave test [1] for neat cement bars, the fact that calcium hydroxide can react with amorphous hydrated calcium silicate already formed, to give the hydrate of tricalcium silicate, is significant. This result, taken in conjunction with those of Mather and Thorvaldson [20], indicates that any expansion which results from autoclaving cannot be caused by crystallization of calcium hydroxide liberated from the cement compounds, but must be ascribed to other causes.

As was pointed out with reference to sand-lime brick, the crystallization of hydrated calcium silicates occurs slowly, requiring days or weeks to reach completion even at temperatures above 200° C. It is not to be expected, therefore, that well-developed crystals of any of the various hydrates described in this paper would be found in specimens steamed for the short period employed in the autoclave test. Only incipient crystallization would occur, but the products should be the same as those formed over longer periods.

V. SUMMARY

Table 11 gives a summary of optical properties of the natural and synthetic minerals identified in this investigation.

X-ray study of the hydrated calcium silicate minerals indicated that the following are distinct compounds:

Okenite	$CaO.2SiO_2.2H_2O$.
Gyrolite	$2CaO.3SiO_2.2H_2O$.
Crestmoreite	$2CaO.2SiO_2.3H_2O$.
Xonotlite	$5CaO.5SiO_2.H_2O$.
Afwillite	$3CaO.2SiO_2.3H_2O$.
Foshagite	$5CaO.3SiO_2.3H_2O$.
Hillebrandite	$2CaO.SiO_2.H_2O$.

Centrallasite, $4CaO.7SiO_2.5H_2O$, and truscottite, $4(Ca,Mg)O.7SiO_2.5H_2O$, seem to be impure forms of gyrolite. Riversideite, $2CaO.2SiO_2.H_2O$, is apparently not a distinct mineral and is probably the same compound as crestmoreite.

Preparations having X-ray patterns identical with those of gyrolite, xonotlite, and foshagite were synthesized by hydrothermal methods. Other compounds formed were cristobalite, wollastonite, pseudowollastonite, β–$3CaO.2SiO_2$, $4CaO.5SiO_2.5H_2O$, $CaO.SiO_2.H_2O$, $2CaO.SiO_2.H_2O$, $10CaO.5SiO_2.6H_2O$, and $3CaO.SiO_2.2H_2O$.

TABLE 11.—*Optical properties of natural and synthetic minerals identified in this study*

Composition	Optical properties					Crystal system and habit	Elongation	Mineral name	Obtained synthetically
	Sign	Optic angle	α or ω	β	γ or ϵ				
$CaO.2SiO_2.2H_2O$	−	Large	1.530		1.541	Orth. fibrous.	+	Okenite	No.
$2CaO.3SiO_2.2H_2O$	−	0	1.548		1.536	Trig. fibrous lamellae.	+	Gyrolite	Yes.
$4CaO.5SiO_2.5H_2O$				1.54		Acicular	+	Tobermorite(?)	Yes.
$5CaO.5SiO_2.H_2O$	+	Small	1.583	1.583	1.594	Orth. (?) fibrous.	+	Xonotlite	Yes.
$CaO.SiO_2.H_2O$				1.603		(?)	−		Yes.
$2CaO.2SiO_2.3H_2O$	−	Large	1.593	1.603	1.607	Fibrous	+	Crestmoreite	No.
$3CaO.2SiO_2.1.5H_2O$				1.60		do			Yes.
$3CaO.2SiO_2.3H_2O$	+	54°	1.617	1.620	1.634	Mon. prism.	−	Afwillite	No.
$5CaO.3SiO_2.3H_2O$	+	Small	1.594	1.594	1.598	Orth. fibrous.	+	Foshagite	Yes.
$2CaO.SiO_2.H_2O$	−	60° to 80°	1.605	1.61	1.612	do	+	Hillebrandite	No.
$2CaO.SiO_2.H_2O$				1.60		(?)	+		Yes.
$2CaO.SiO_2.H_2O$				1.64		(?)			Yes.
$10CaO.5SiO_2.6H_2O$	+	Medium	1.614	1.620	1.633	Orth	+		No.
$6CaO.3SiO_2.2H_2O$			1.642		1.672	(?)			Yes.
$3CaO.SiO_2.2H_2O$			1.590		1.602	Fibrous	+		Yes.

Attempts to produce okenite synthetically were unsuccessful. Thus, a sample of calcium disilicate glass treated with water for 8 weeks at 150° C gave partial crystallization to cristobalite only.

Gyrolite was formed at 150° to 400° C from glasses and amorphous hydrates having CaO/SiO_2 molar ratios in the vicinity of 2:3.

Treating amorphous hydrate with CaO/SiO_2 molar ratio 0.80 at temperatures between 150° and 275° C gave a single phase of distinctive X-ray pattern, and a composition corresponding to $4CaO.5SiO_2.5H_2O$. This composition is similar to that reported for the rare mineral tobermorite. At 300° C the product was xonotlite.

Amorphous monocalcium silicate hydrate at 150° C crystallized to $CaO.SiO_2.H_2O$, which had a distinctive X-ray pattern. However, in the presence of higher molar ratios of lime to silica, $CaO.SiO_2.H_2O$ was formed at temperatures as high as 350° C.

Xonotlite, $5CaO.5SiO_2.H_2O$, crystallized from preparations of amorphous hydrated monocalcium silicate between 165° ±15° C and 395° ±5° C (70 to 225 atm). Above 395° C wollastonite crystallized.

Amorphous hydrate of molar ratio $3CaO/2SiO_2$ treated between 150° and 400° C did not yield afwillite, $3CaO.2SiO_2.3H_2O$, but instead crystallized partially to $CaO.SiO_2.H_2O$ at the lower temperatures and to xonotlite at the higher. These were probably metastable crystallizations resulting from the relatively high crystallization potential of the monocalcium silicate hydrates. Anhydrous tricalcium disilicate treated at 250° C was converted to an unidentified hydrate.

The usual form of anhydrous tricalcium disilicate treated at 500° C (380 atm) for 2 weeks was converted to a low-temperature or β form of the anhydrous compound. It inverts to the high-temperature form at 1,024° ±5° C.

Glass of composition $5CaO.3SiO_2$ treated at 300° and 350° C was converted to a product having an X-ray pattern identical with that of the mineral foshagite.

The compound $10CaO.5SiO_2.6H_2O$ was formed from β- and γ-dicalcium silicates, tricalcium silicate, and mixtures of lime and silica gel in the temperature range 100° to 200° C. Attempts to prepare a hydrate identical with natural hillebrandite were unsuccessful.

Tricalcium silicate treated with water between 200° and 450° C hydrated directly to $3CaO.SiO_2.2H_2O$. No hydrates of higher lime content than $3CaO.SiO_2.2H_2O$ appear to exist.

A number of unsuccessful attempts were made to isolate and identify the cementing material in sand-lime brick.

The authors gratefully acknowledge their indebtedness to Herbert Insley for his assistance in the X-ray and microscopic studies, to W. F. Foshag of the United States National Museum for supplying samples of most of the naturally occurring minerals, and to E. S. Newman for carrying out the experiments on sand-lime brick.

VI.—REFERENCES

[1] *Report of Committee C-1 on Cement.* Proc. Am. Soc. Testing Materials **37,** 290 (1937).

[2] G. Grime and G. E. Bessey, *The cementing material of sand-lime bricks. An X-ray and microscopic examination,* Ceram. Soc. Trans. **32** [1], 14 (1933).

[3] J. W. Mellor, A comprehensive treatise on inorganic and theoretical chemistry, **6,** 358 (Longmans, Green and Co., New York, N. Y., 1925).

[4] A. S. Eakle, *Minerals associated with the crystalline limestone at Crestmore, Riverside County, Calif.,* Univ. of Calif. Bul. Dept. Geology **10,** 327 (1917).

[5] V. A. Vigfusson, *The hydrated calcium silicates.* I. *The system* $CaO-SiO_2-H_2O$. II. *Hillebrandite and foshagite,* Am. J. Sci. **21,** 67 (1931).

[6] E. P. Flint and L. S. Wells, *Study of the system* $CaO-SiO_2-H_2O$ *at 30° C and of the reaction of water on the anhydrous calcium silicates,* BS J. Research **12,** 751 (1934) RP687.

[7] G. W. Morey and C. N. Fenner, *The ternary system* $H_2O-K_2SiO_3-SiO_2$. J. Am. Chem. Soc. **39,** 1173 (1917). G. W. Morey and Earl Ingerson, *A bomb for use in hydrothermal experimentation,* Am. Mineral. **22,** 1121 (1937).

[8] C. J. van Nieuwenburg and H. B. Blumendal, *The isotherms of water from 350° to 480° C and for pressures up to 600 kg/cm²,* Rec. trav. chim. **51,** 707 (1932).

[9] G. W. Morey and Earl Ingerson, *The pneumatolytic and hydrothermal alteration and synthesis of silicates,* Econ. Geology **32,** 629 (1937).

[10] M. Schlaepfer and P. Niggli, *Neue Beitrage zur hydrothermalen Silikatbildung,* Z. anorg. Chem. **87,** 52 (1914).

[11] E. Baur, *Ueber hydrothermale Silikate.* Z. anorg. Chem. **72,** 119 (1911).

[12] M. F. Heddle, *Preliminary notice on substances which may prove to be minerals,* Min. Mag. **4,** 119 (1880).

[13] P. Groth, *Tabellarische Uebersicht der Mineralien,* Munich and Berlin (1921).

[14] C. J. van Nieuwenburg and H. B. Blumendal, *The pneumatolytic synthesis of silicates,* I. Rec. trav. chim. **50,** 129 (1931).

[15] S. Nagai, *Hydrothermale Synthesen von Calciumsilikaten,* II, Z. anorg. Chem. **207,** 321 (1932).

[16] W. Kohler, *Ueber die Bildung kristallisierter Kalziumsilikathydrate,* Tonind. Ztg. **59,** 739; 754 (1935).

[17] T. Thorvaldson and G. R. Shelton, *Steam curing of portland cement mortars. A new crystalline substance.* Can. J. Research **1,** 148 (1929).

[18] V. A. Vigfusson, G. N. Bates, and T. Thorvaldson, *Hydrothermal synthesis of calcium hydrosilicates.* Can. J. Research **11,** 520 (1934).

[19] N. B. Keevil and T. Thorvaldson, *The hydration of dicalcium silicate and tricalcium silicate,* Can. J. Research **14,** 20 (1936).

[20] D. T. Mather and T. Thorvaldson, *The action of saturated steam on dicalcium ferrite and tetracalcium aluminoferrite,* Can. J. Research **15** [B] 331 (1937).

WASHINGTON, August 19, 1938.