U.S. DEPARTMENT OF COMMERCE
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Upper Atmosphere and Space Physics. Upper Atmosphere and Plasma Physics. Ionosphere and Exosphere Scatter. Airglow and Aurora. Ionospheric Radio Astronomy.

Radio Physics.

Circuit Standards.

WVMP SAR Reference 3-23

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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.

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III. Hydrothermal synthesis of hydrated calcium silicates—Continued. Page
4. Hydrothermal treatment of calcium silicates of varying molar ratios of lime to silica—Continued.

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.

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[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

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[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

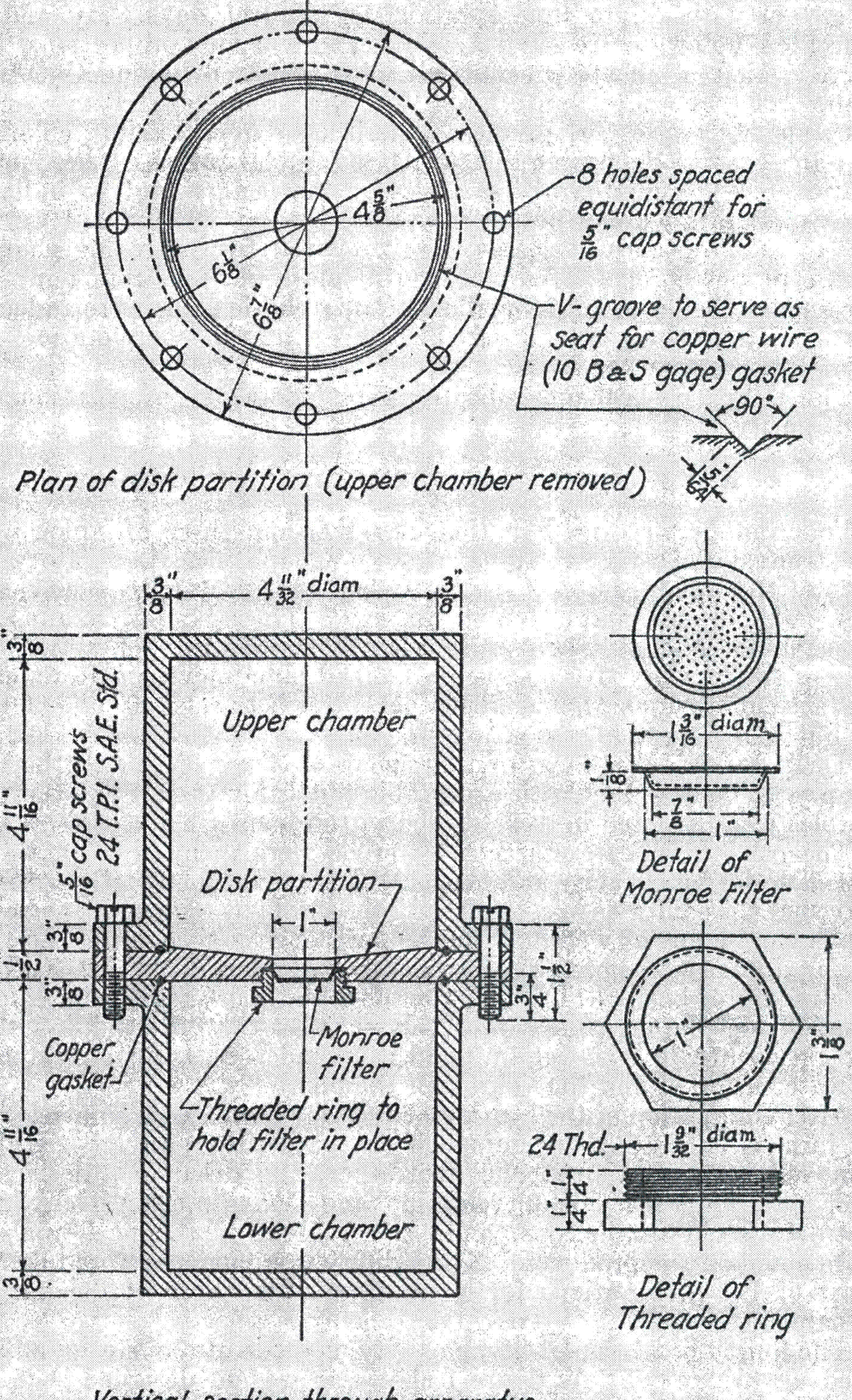

FIGURE 1.—*Bomb for hydrothermal synthesis (in position for filtering).*

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.

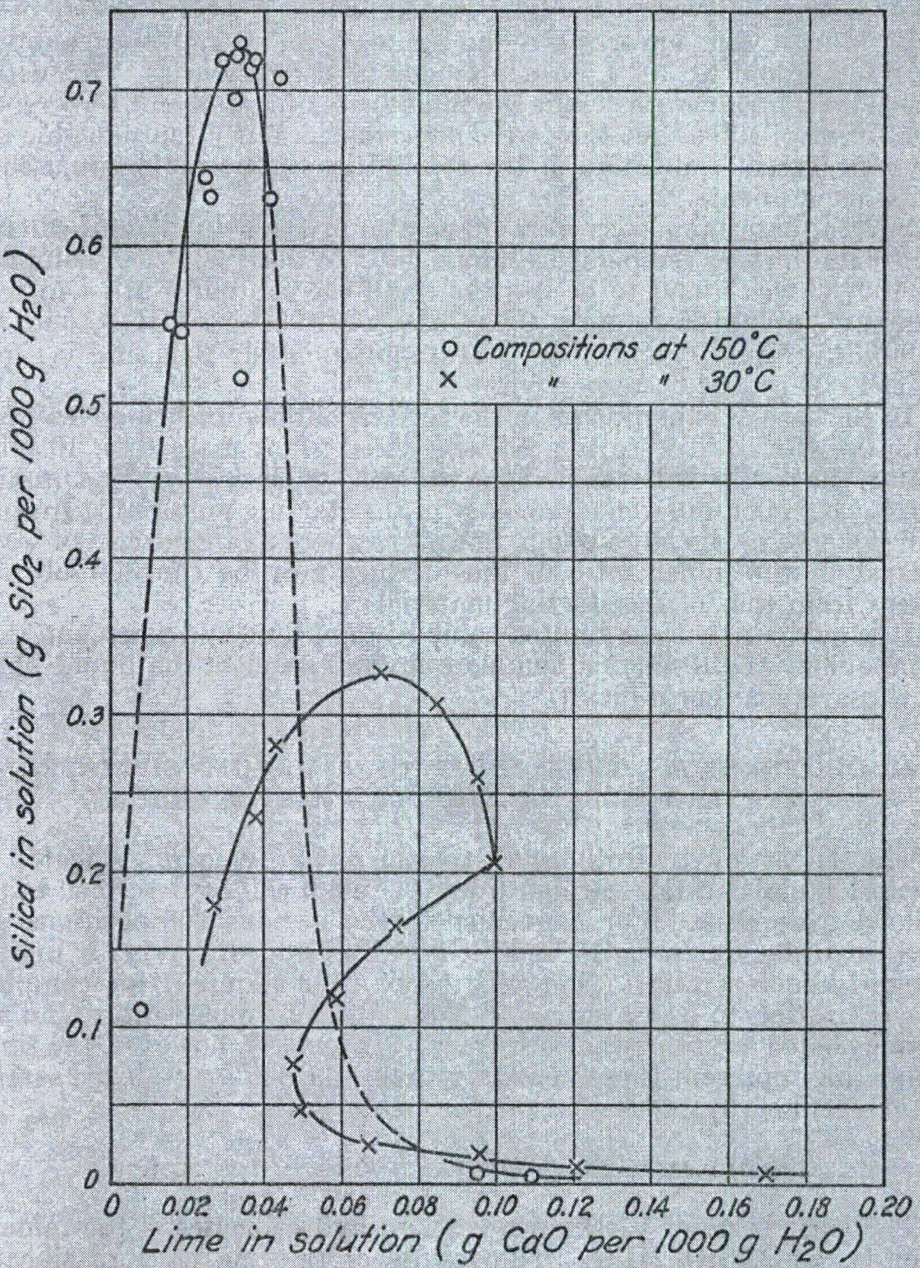

FIGURE 2.—*Solubilities of silica in lime solutions at 30° and 150° C.*

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.

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[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.

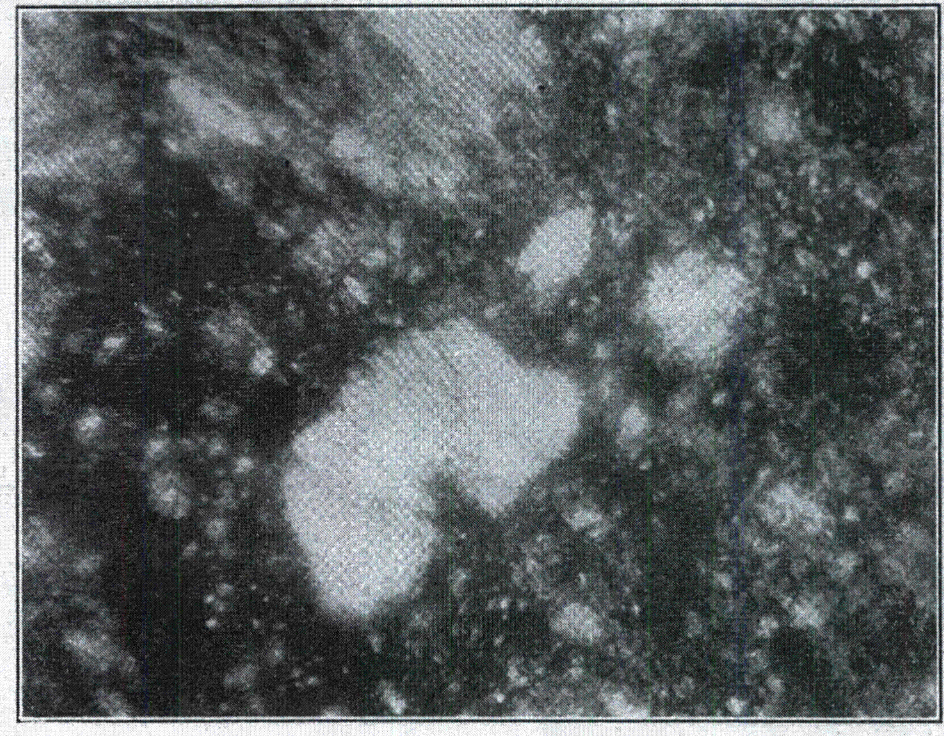

FIGURE 3.—*Synthetic gyrolite.*

Crossed nicols, magnification ×180

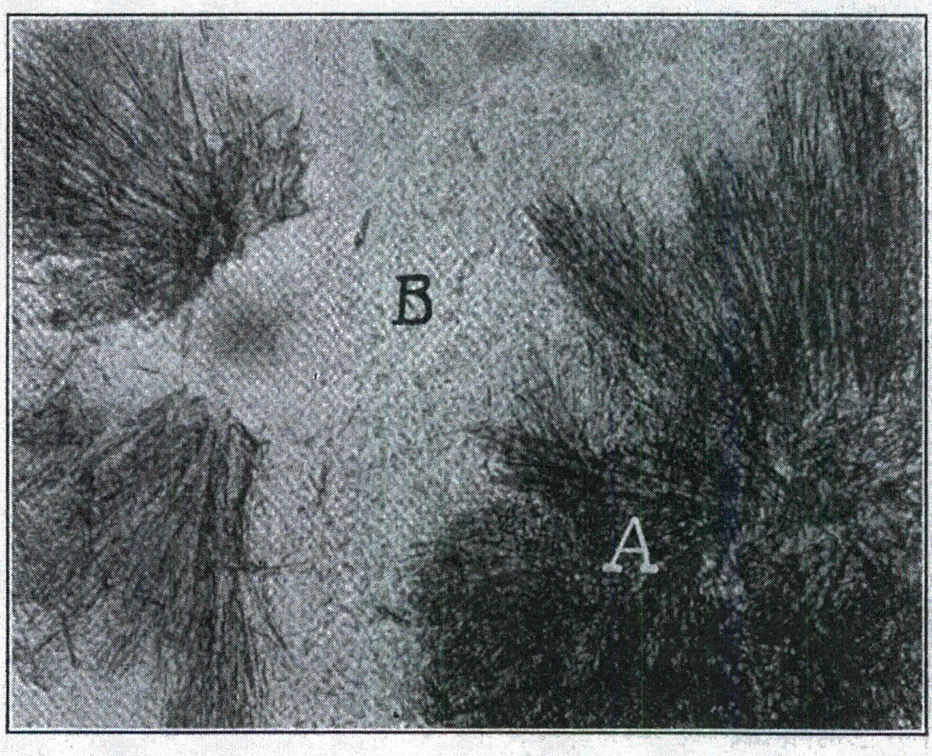

FIGURE 4.—*Synthetic (A) xonotlite + (B) gyrolite.*

Magnification ×180.

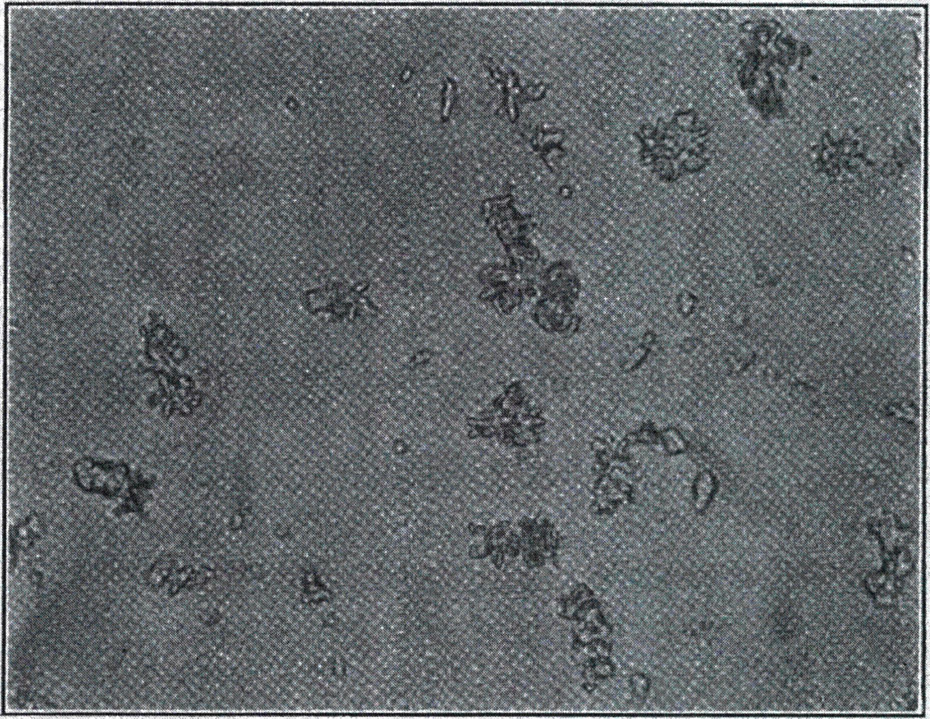

FIGURE 5.—*Synthetic* $CaO.SiO_2.H_2O$.
Magnification ×900.

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	$\beta.3CaO.2SiO_2$.

FIGURE 7.—*Synthetic wollastonite.*
Magnification ×180.

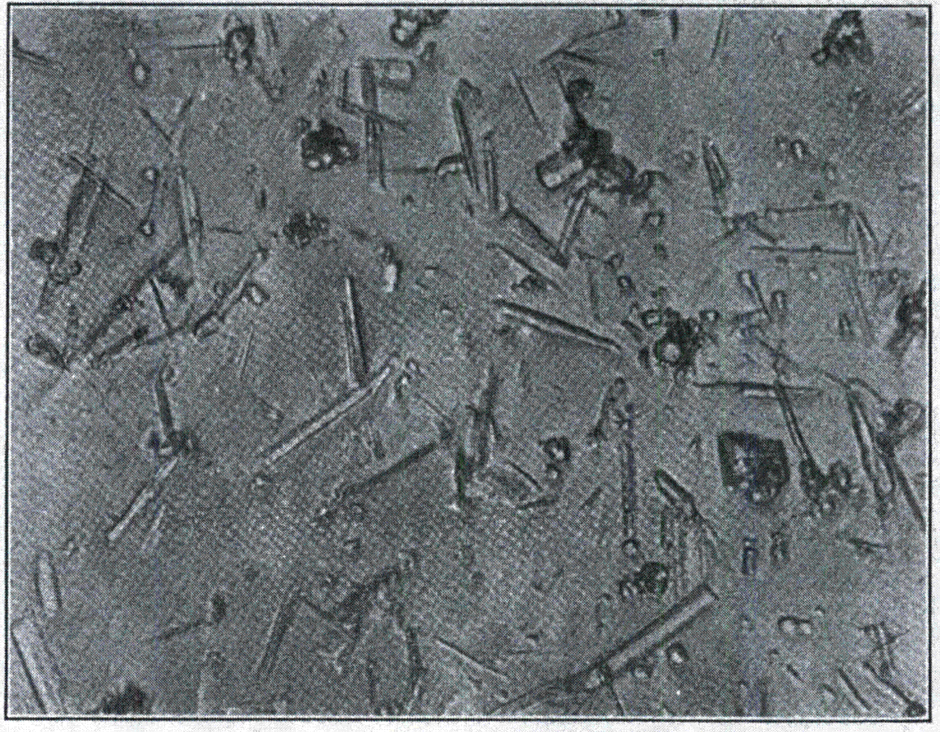

FIGURE 8.—*β-tricalcium disilicate.*
Magnification ×900.

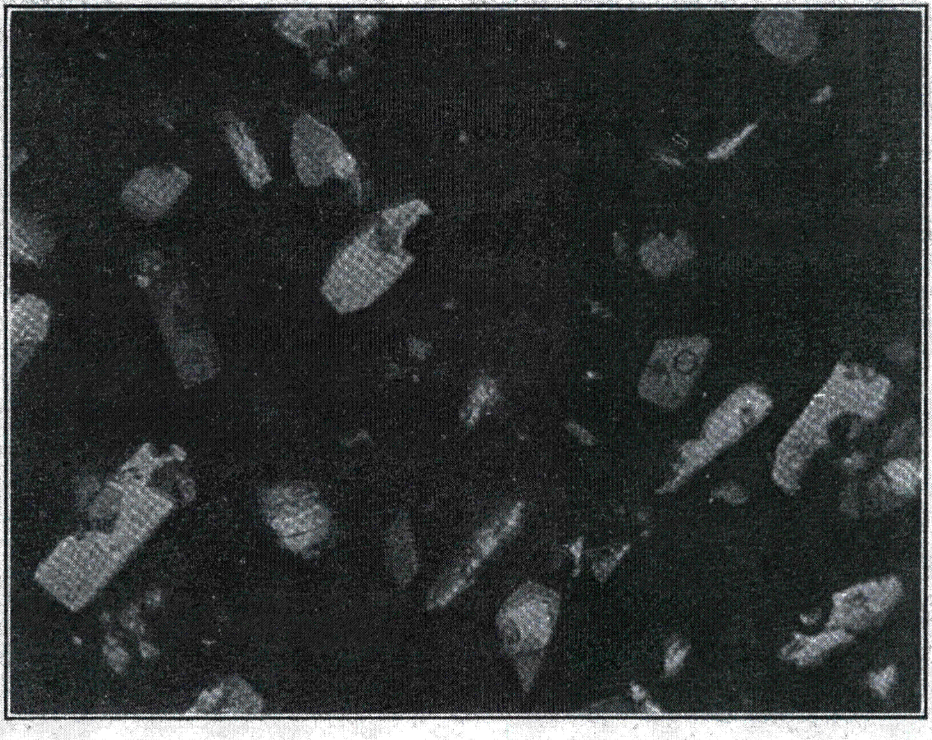

FIGURE 9.—*Synthetic* $10CaO.5SiO_2.6H_2O$.

Crossed nicols, magnification ×400.