ART. VII.—*The Ternary System CaO-MgO-SiO_2*; by J. B. FERGUSON and H. E. MERWIN.

CONTENTS.

Introduction.
Previous investigations: Temperature relations and optical properties.
General procedure and apparatus.
The crystalline phases: Composition, optical properties, etc.
Fields of stability.
Temperature relations along the boundary lines.
The quintuple points.
Melting temperatures within the fields.
Discussion of the fields.
    Pseudowollastonite, wollastonite, $5CaO.2MgO.6SiO_2$, diopside.
    Monticellite solid solutions.
    Åkermanite.
The tridymite-cristobalite inversion.
The binary systems within the ternary system.
Summary.

INTRODUCTION.

A number of investigations dealing with one or more of the four oxides, lime, alumina, magnesia and silica, have in recent years been carried out as preliminary steps in the laboratory study of rocks. To the results of these investigations which dealt with the three ternary systems, CaO-Al_2O_3-SiO_2, CaO-MgO-Al_2O_3, MgO-Al_2O_3-SiO_2, and parts of the fourth ternary system, CaO-MgO-SiO_2, we wish to add the results[1] of an investigation of the hitherto unknown parts of this last system and also to correlate these results with those previously obtained by others. Since but four ternary systems may be constructed from the four oxides, this investigation marks the completion of the series of studies of the solidus-liquidus relations in these ternary systems.

[1] A short preliminary summary of these results was published in Proc. Nat. Acad. Sci., 5, 16, 1919.

PREVIOUS INVESTIGATIONS.

A somewhat brief review of the results of the earlier workers in this field will be given. The component oxides will be considered first.

Lime, CaO.

The melting point of lime has been determined by Kanolt[2] as 2570°. Two crystalline modifications, both isometric, appear to exist;[3] the one found at ordinary temperatures has perfect cubic cleavage and a refractive index of 1·83.[4] In the ternary melts it has always appeared in rounded grains.[4]

Magnesia (periclase), MgO.

Kanolt[5] places the melting point of magnesia at 2800°C. Only one crystalline form is known, which is isometric, with perfect cubic cleavage and refractive index[6] of about 1·737. It has been observed in melts as rounded grains, sharp octahedrons or cuboctahedrons, and skeletal octahedrons.[7]

Silica, SiO_2.

The several crystalline forms of silica have been thoroughly investigated by C. N. Fenner.[8] Of these only tridymite and cristobalite occur as primary phases in this ternary system. *Tridymite* appears as thin plates[9] or platy aggregates[10] having refractive indices[11] of $a = 1·469$, $\gamma = 1·473$.[12] *Cristobalite* appears as aggregates,[10] octahedra and cubes:[9] $a = 1·484$, $\gamma = 1·487$.[8] It melts at $1710 \pm 10°C$.[12] The sluggish transition between cristo-

---

[2] J. Wash. Acad. Sci., 3, 315, 1915.

[3] For summary of evidence see J. Wash. Acad. Sci., 5, 567, 1915.

[4] Rankin and Wright, this Journal (4), 39, 1, 1915; Sosman, Hostetter, and Merwin, J. Wash. Acad. Sci., 5, 566, 1915.

[5] J. Wash. Acad. Sci., 3, 315, 1915.

[6] Slight differences in refractive index indicate solid solution under some conditions. Mallard, Bull. Soc. Min. Fr., found 1·7364; Wright, this Journal (4), 28, 325, found 1·734 ± ·002; Sommerfeldt, Centralbl. Min. Geol. Pal., 1907, 213, found 1·7350. We have found 1·7375 for some fused magnesia of optical quality furnished by the Alundum Co. The dispersion of this sample follows: C = 1·7335, F = 1·7475.

[7] Definite crystals have been observed during this study. See also Rankin and Merwin, J. Am. Chem. Soc., 38, 570, 1916.

[8] This Journal (4), 36, 331, 1913.

[9] N. L. Bowen, this Journal (4), 38, 245, 1914.

[10] G. A. Rankin and F. E. Wright, this Journal (4), 39, 1, 1915.

[11] Fenner's values were confirmed by Schaller, when account is taken of the higher values—probably caused by solid solution—observed for this natural material. See note 12 below.

[12] J. B. Ferguson and H. E. Merwin, this Journal, 46, 417, 1918.

balite and tridymite[13] takes place in this system below 1500°C.; for the pure substances Fenner's value is 1470 ± 10°C.

The System lime-magnesia, CaO-MgO.

In this system a simple eutectic relation exists. The eutectic composition is CaO 67, MgO 33, and its temperature about 2300°C. The diagram given by Rankin and Merwin[14] is partially reproduced in fig. 1.

The System lime-silica, CaO-SiO₂.

This system is somewhat more complicated. Four compounds are known to exist. They are the calcium metasilicate, the tricalcium disilicate, the calcium ortho-silicate and the tricalcium silicate. The meta- and ortho-silicates only are stable at their melting points and the tricalcium silicate does not even occur as a primary phase in this binary system. Two forms of the metasili-cate, wollastonite and pseudowollastonite are known and also three forms of the orthosilicate. The temperature relations existing in this system are given in fig. 2 which is a corrected reproduction of the major part of the diagram given by Rankin and Wright.[15] The corrections deal with the melting point of cristobalite and the extent of the metasilicate solid solution.

The following are the optical properties observed for the phases in this binary system which occur in the ternary system.

Pseudowollastonite,[16] $aCaO.SiO_2$; pseudohexagonal equant grains, polysynthetic twinning common; nearly uniaxial $+$, $a = 1.610$, $\beta = 1.611$, $\gamma = 1.654$; extinction angles small.

Wollastonite,[16, 17] $\beta CaO.SiO_2$; monoclinic, lath-shaped; cleavage parallel to elongation; $a = 1.616$, $\beta = 1.629$, $\gamma = 1.631$, 2E about 70°; extinction parallel, optic plane normal to cleavage lines.

$3CaO.2SiO_2$; probably orthorhombic, equant grains; $a = 1.641$, $\gamma = 1.650$; $+ 2V$ large.

a *calcium orthosilicate*, $2CaO.SiO_2$, is stable from its

[13] This inversion is discussed on page 118 of this paper.
[14] G. A. Rankin and H. E. Merwin, J. Am. Chem Soc., 38, 568, 1916.
[15] This Journal, 39, 1, 1915.
[16] For later observations, see pp. 91, 92.
[17] Day, Shepherd, Wright, this Journal 22, 290-291, 1906.

FIG. 1.
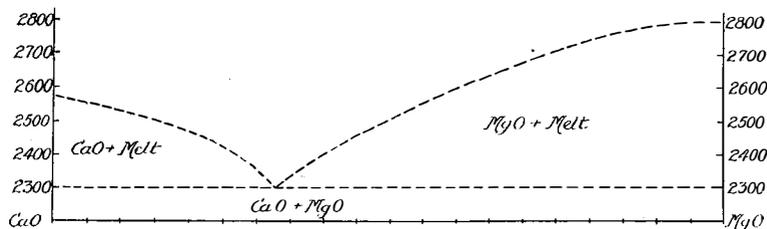
FIG. 1.—The binary system CaO-MgO. weight per cent.

FIG. 2.
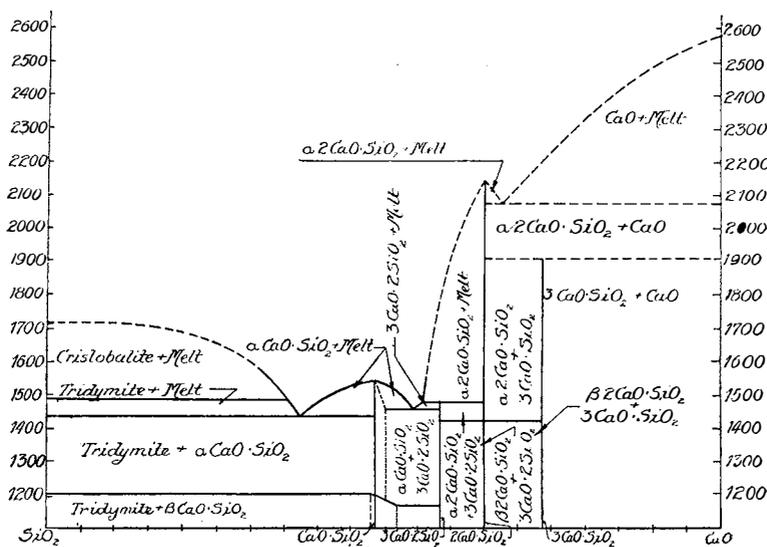
FIG. 2.—The binary system CaO-SiO₂. weight per cent.

FIG. 3.
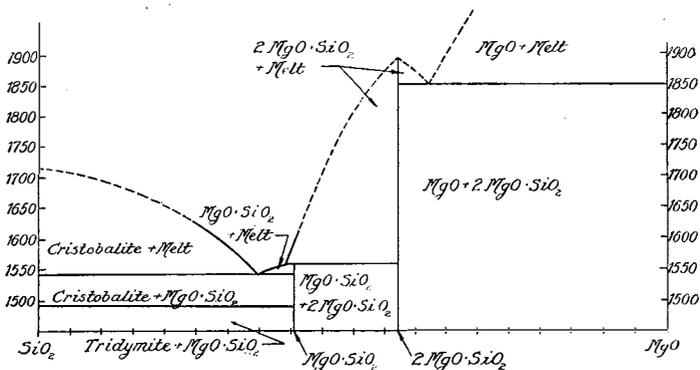
FIG. 3.—The binary system MgO-SiO₂. weight per cent.

melting point to 1420°.[18]   The grains tend toward prismatic habit, are characteristically twinned, have $+ 2V$ large, $a = 1\cdot715$, $\beta = 1\cdot720$, and $\gamma = 1\cdot737$.[19, 20]

β *calcium orthosilicate* is stable from 1420° to about 675°.[18, 23]   The habit and optical properties are practically the same as for the a-form except that twinning is seldom present ($a = 1\cdot717$, $\gamma = 1\cdot735$).[19, 21]

In the binary system $CaO\text{-}SiO_2$, the inversion a to β orthosilicate takes place promptly if the inversion temperature is passed through not very rapidly.[22]

γ *calcium orthosilicate* is stable below 675°.[23]   It has prismatic habit, $a = 1\cdot642$, $\beta = 1\cdot645$, $\gamma = 1\cdot654$, $+ 2V =$ about 60°.[24]

The System magnesia-silica, $MgO\text{-}SiO_2$.

Two binary compounds occur in this system, the metasilicate and the orthosilicate.   The former is unstable at its melting point, while the latter is stable.   The temper-
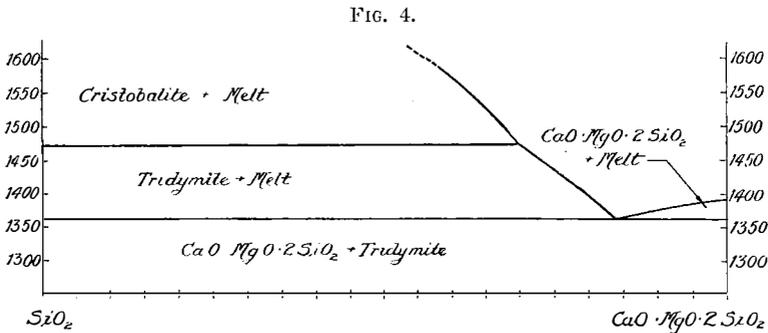
Fig. 4.

FIG. 4.—The binary system SiO_2-$CaO.MgO.2SiO_2$, wt. per cent.

[18] Rankin and Wright, this Journal, 39, 76, 1915.

[19] Ibid., p. 7.

[20] Observations during the present study on crystals from various parts of the a orthosilicate field, confirm these data except that β is about 0·003 larger, and in some quenches scarcely a twinned grain could be found (see note 22), and the elongation may be either positive or negative.

[21] No accurate measurements of refractive index of this form were made during the present study.

[22] In most if not all of the quenches of the ternary system here considered which contained the a form as a primary phase, the a form has apparently persisted for many months. This is true unless either the criterion of twinning is not sufficient for distinguishing this form; or the inversion is like that of quartz at 575° and leaves no distinguishable optical effects. (See note 20.)

[23] Day, Shepherd and Wright, this Journal, 22, 281, 1906.

[24] Corrected values (see note 19).

ature relations are shown in fig. 3. This is a reproduction of the diagram given by Bowen and Andersen[25] upon which the melting point of cristobalite has been corrected. The following descriptions of these compounds are given by the same investigators.

Clino-enstatite, $MgO.SiO_2$, Monoclinic; polysynthetic twinning after (100) is exceedingly characteristic.[26] The plane of the optic axis is normal to (010). The angle. $\gamma_\wedge c = 22°$. Refractive indices: $a = 1.651$, $\gamma = 1.660$.
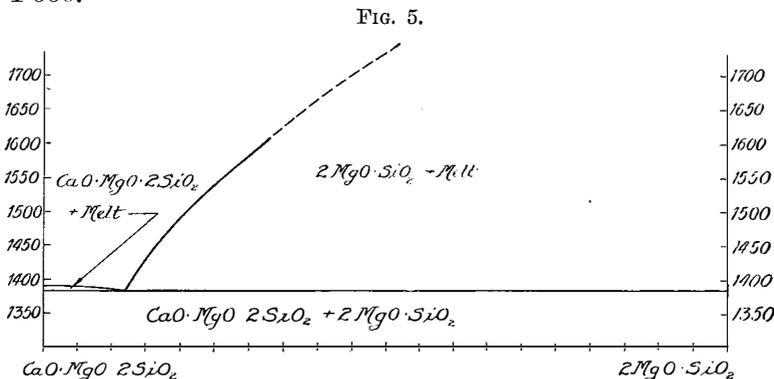
FIG. 5.

FIG. 5.—The binary system 2MgO.SiO₂-CaO.MgO.2SiO₂. wt. per cent.

Forsterite, $2MgO.SiO_2$. $a = 1.635_1$, $\beta = 1.651_0$, $\gamma = 1.670$; $2V = 85°16'$. Optically positive.[27]

Partial Studies of Ternary System $CaO\text{-}MgO\text{-}SiO_2$.

Besides these binary systems dealing with the oxides, several systems have been studied which form part of the ternary system itself. (See fig. 5.) The first of these systems is the system $CaO.SiO_2$-$MgO.SiO_2$. This system may be divided into two parts, the ternary compound $CaO.MgO.2SiO_2$, called diopside, representing the point of division. Of the two resultant systems, the system $CaO.MgO.2SiO_2$-$MgO.SiO_2$ has been shown by Bowen to be not a true binary system and will be discussed when our later work is considered. The system $CaO.MgO. 2SiO_2$-$CaO.SiO_2$ was first studied by Allen, White, Wright and Larsen[28] and their results were interpreted

[25] N. L. Bowen and Olaf Andersen, this Journal (4), 37, 487, 1914.
[26] In ternary melts with magnesia, twinning may be rare, this Journal, 45, 302, 1918.
[27] Allen, Wright, and Clement, this Journal, 22, 391, 1906.
[28] This Journal (4), 27, 1, 1909.

by Boeke.[29]   The method used was that of heating curves
(the quench method has not been perfected) and was
scarcely adequate.   Many curves were obtained which
were susceptible of various interpretations.   The most
probable interpretation was based upon the assumption
that the inversion temperature of the wollastonite was
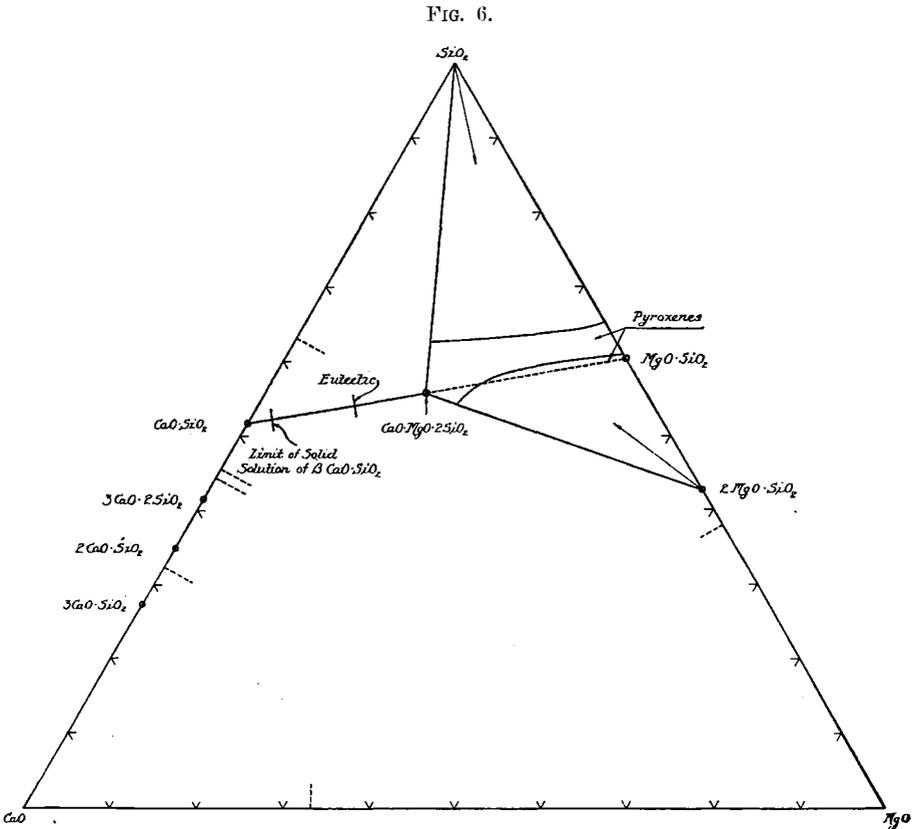
FIG. 6.

FIG. 6.—Partial ternary diagram showing the previously published results:
wt. per cent.

never raised enough by solid solution to cause the solid
solutions to appear as primary phases.

The chief optical properties observed for diopside are
as follows :[30]

$\alpha = 1\cdot664\text{-}6,\ \beta = 1\cdot671\text{-}3,\ \gamma = 1\cdot694\text{-}5;\ +2V = 59°;\ \gamma_\wedge\acute{c}$
$= 38\frac{1}{2}°.$

[29] Grundlagen der physikalisch-chemischen Petrographie, 182, 1915.
[30] Including new determinations.

The two systems SiO_2-$CaO.MgO.2SiO_2$ and $CaO.MgO.$
$2SiO_2$-$2MgO.SiO_2$ have been studied by Bowen[31] as part
of the ternary system diopside-forsterite-silica. They
show simple eutectics, as may be seen in the diagrams
given in figs. 4 and 5.

But in his ternary system Bowen found that there
existed a complete series of solid solutions having diop-
side and clino-enstatite as end members.[32]   Most of these
solutions, like clino-enstatite, are unstable at their melt-
ing points.   The rather complicated relations which
obtain as a result of this somewhat unusual condition
will not be discussed here but may be found in the orig-
inal paper.

The concentration relations in these systems in so far
as they affect the ternary system CaO-MgO-SiO_2 are
collectively shown on the triangular diagram given in fig.
6 and form the starting point of the present investiga-
tion.

GENERAL PROCEDURE.

The initial step in a research of this character is the
preparation of charges of known composition, and for
this purpose chemically pure calcium carbonate, magne-
sium carbonate and silica were used.   The magnesium
carbonate was not used directly in this process but was
first calcined in a platinum crucible in a Fletcher gas-
blast furnace.   After the ingredients were weighed out
and thoroughly mixed in a mortar, the mixtures were
fused in platinum crucibles and then reduced to a fine
powder.   This process was repeated two or three times
to ensure complete homogeneity in the final product.
Mixtures which fused completely at temperatures below
1500°C were heated in a platinum-resistance furnace;
those melting at higher temperatures, in a Fletcher gas-
blast furnace.   When possible the compositions were
finally prepared as glasses, since this form of material
is necessary in many experiments and in addition may
be easily tested under the microscope for homogeneity.

A few peculiarities were noted during the preparation
of the compositions.   Those lying within the silica field,
unless they rapidly cooled, gave either milky or porce-
lain-like glasses.   In the porcelain-like glasses in which
the crystallization was further advanced, crystals of

[31] This Journal (4), **38**, 207, 1914.
[32] See p. 92.

silica could be identified, but in the milky glasses the particles causing the milkiness could not be identified microscopically. In the charges very rich in silica this tendency to crystallize was accompanied by a great viscosity, so that relatively large crystals of cristobalite,

FIG. 7.
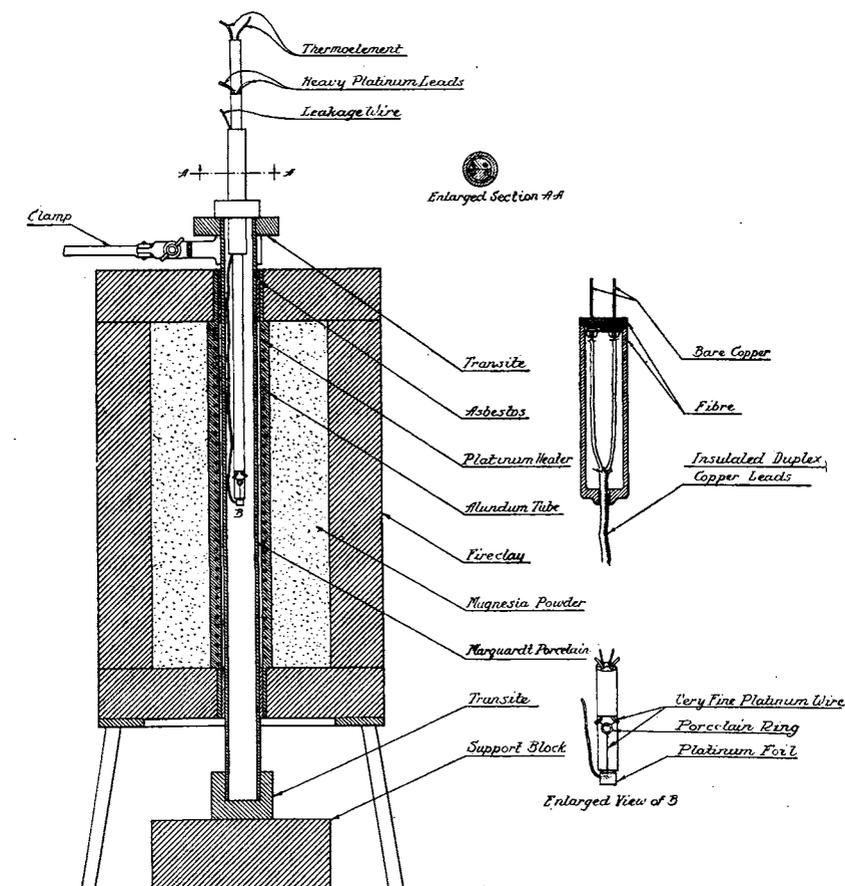
FIG. 7.—The quenching apparatus and furnace. (1) The furnace set up: (2) Enlarged views of parts of the quenching apparatus showing the method of insulating leads, etc., and the method of attaching the charge: (3) a longitudinal section of the device used to carry the copper leads by means of which a heavy current could be sent through the platinum leads to which the charge is attached and thus cause the charge to fall by fusing the supporting fine platinum wire. When this operation is to take place, the support block and transite cap are removed and a dish containing mercury is inserted beneath the marquardt porcelain tube in order to catch the charge and chill it instantly.

once formed, would dissolve but slowly, thus making almost impossible the preparation of homogeneous compositions. Compositions lying within the magnesia field showed a similar tendency to crystallize, and with these also, difficulty was experienced in obtaining homogeneity.

Once prepared, each composition was thoroughly investigated by means of the quenching method. This method consists in holding a small quantity of a given composition (called a "charge") at a given temperature long enough to insure the attainment of equilibrium and then chilling it suddenly without disturbing this equilibrium condition. The charge is wrapped in a small piece of platinum foil 0·01 m.m. thick which is attached to a thermoelement tube in such a manner as to be very near the junction, and is dropped into mercury by fusing the supporting wire by means of an electric current. The details of the method may be found in several of the preceding papers.[33] The apparatus is shown in fig. 7.

A few compositions, thoroughly investigated, served to locate approximately the various boundary lines, and with this information the efficient selection of the subsequent compositions was an easy task. Most of the charges required from 20 to 30 minutes to reach an equilibrium condition, but some charges, notably those in the $2CaO.MgO.2SiO_2$ field and those containing much silica, required a much longer treatment. Charges in which at equilibrium there was no glass, such as those used in the study of the wollastonite solid solutions, were heated for days before samples suitable for microscopic examination could be obtained. The formation of unstable pseudowollastonite crystals at temperatures below but near the inversion temperature took place readily when suitable glasses were crystallized at these temperatures. The inversion of pseudowollastonite to wollastonite does not take place readily and so when charges of wollastonite free from pseudowollastonite were desired, glasses were first crystallized at temperatures ranging from 800 to 900°C over long periods of time (15 hours) and this material if free from pseudowollastonite (in not more than one-half of the charges was this true) and from glass was then reheated at higher temperatures for some hours in order to let the crystals grow and enable a final selection of material to be made with certainty.

[33] See this Journal, 39, 1, 1915.

Charges within the monticellite ($CaO.MgO.SiO_2$) field, and in the forsterite field near it, crystallized with such rapidity that great difficulty was experienced in quenching them. The resorption of magnesia did not occur readily and charges selected for a study of this phenomenon were prepared in such a manner as to prevent the formation of large crystals of magnesia which if formed would not then dissolve in a reasonable time. The microscopic examinations were in part very troublesome. It often happened that the crystalline phases were not only very similar optically but also had nearly the same refractive index as the glass in which they were imbedded, thus making the positive identification of traces of either almost impossible.

The Crystalline Phases.

The following crystalline phases[34] are found in the ternary system stable in contact with a suitable melt:

1. Lime. CaO.
2. Periclase, MgO.
3. Cristobalite and tridymite, SiO_2.
4. Pseudowollastonite, $aCaO.SiO_2$.
5. $3CaO.2SiO_2$.
6. $a2CaO.SiO_2$ and $\beta2CaO.SiO_2$.
7. Clino-enstatite, $MgO.SiO_2$.
8. Forsterite, $2MgO.SiO_2$.
9. Diopside, $CaO.MgO.2SiO_2$.
11. Åkermanite, $2CaO.MgO.2SiO_2$.
11. $5CaO.2MgO.6SiO_2$.
12. Monticellite ($CaO.MgO.SiO_2$)—forsterite solid solutions.
13. Wollastonite-diopside solid solutions.
14. Wollastonite-$5CaO.2MgO.6SiO_2$ solid solutions.

The significant properties of all of these phases with the exception of the compounds $5CaO.2MgO.6SiO_2$, and $2CaO.MgO.2SiO_2$ and the solid solutions of wollastonite, of $5CaO.2MgO.6SiO_2$, and of monticellite, have been given earlier in this paper and only corrections and such additional information as we have obtained will be given here.

Pseudowollastonite grows in remarkably large crystals as it forms during the inversion of wollastonite in the

[34] The general temperature-concentration relations of wollastonite, pseudowollastonite and $5CaO.2MgO.6SiO_2$ will be discussed in detail in a subsequent paper.

solid state, and the characteristic polysynthetic twinning with extinctions of 3° on either side is present. Solid solution represented by about 3 per cent magnesia does not appreciably change its optical properties, except to lower γ about ·006.

Wollastonite: Crystals containing the maximum amount of diopside at the high temperatures (about 17 per cent) in solid solution had the following observed optical properties: $a = 1·619$, $\beta = 1·631$, $\gamma = 1·634$, $- 2V = 40°-65°$. Mixcrystals of wollastonite and $5CaO.2MgO.6SiO_2$, and also $2CaO.MgO.2SiO_2$, have optical properties which are intermediate, so far as they have been determined. Crystals in the middle of the latter series are optically positive with large axial angle.

5CaO.2MgO.6SiO₂: Irregular, elongated grains, β parallel to elongation; $a = 1·621$, $\beta = 1·627$, $\gamma = 1·635$, $+ 2V =$ about 80°.

2CaO.MgO.2SiO₂: Appears in stubby prisms occasionally have definite octagonal cross-section. Crystals from melts of various compositions have $\omega = 1·631 \pm ·002$, $\epsilon = 1·638 \pm ·002$. Frequently the crystals did not appear unless the melt was considerably undercooled. The relation of this compound to åkermanite is discussed later.

Monticellite: The crystals of monticellite appeared as equant grains without facets, and only optical and chemical relationships have been established between the crystals and the natural mineral. The observed values of a were 1·638 to 1·640, of β 1·646, and of γ 1·651 to 1·655; $+ 2V = 85°$ to 90°. These were obtained from five quenches at temperatures between 1400° and 1500°, having compositions ranging from 33 to 37 CaO, 21 to 28 MgO, and 39 to 42 SiO_2.

Diopside: The refractive indices of pure diopside were observed as follows: $a = 1·666$, $\gamma = 1·695$.

Diopside-clinoenstatite solid solutions have not been studied further, but in the application of Mallard's formula to their extinction-angles volume per cent not mol. per cent should have been used.[35]

LIMITS OF THE FIELDS OF STABILITY.

Any charge with a composition in a ternary system similar to the one under investigation may be heated

[35] This Journal (4), **38**, 248, 1914.

until it contains at equilibrium mere traces of crystalline matter immersed in a liquid. This crystalline material may consist of one, two or three phases. Compositions which under these conditions contain one crystalline phase will form an area; those which contain two crystalline phases will form a line, and those which contain three such phases will be points on a triangular concen-
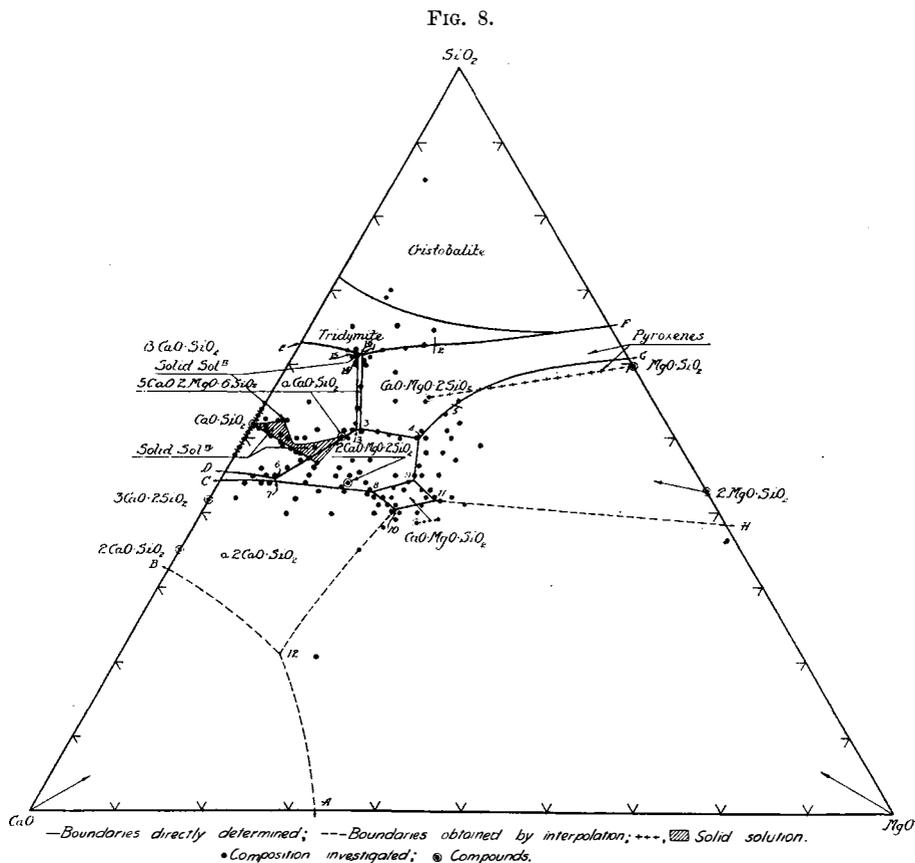
FIG. 8.

FIG. 8.—The triangular concentration diagram giving the compositions investigated and the limits of the fields of stability of the various phases in wt. per cent.

tration diagram. The area belonging to any crystalline phase is called its field of stability, and the lines and points just referred to represent the boundaries of the fields. The fields of stability and the compositions of the charges used to determine their limits are shown in fig. 8. Table I presents the results upon which this diagram is based.

TABLE I.

Quenches which locate the boundaries of the fields of stability.

Composition wt. % CaO	MgO	SiO₂	Temp. °C.	Time in min.	Phases present[36]	Boundary
31	7	62	1343	20	Glass + trace SiO₂	15, E
32	6	62	1370	15	Glass + αCaO.SiO₂	
23	14·5	62·5	1369	20	Glass + trace SiO₂	1, 2
25·25	12·5	62·25	1350	20	Glass + trace SiO₂ + trace CaO.MgO.2SiO₂	
28	10	62	1343	20	Glass + trace SiO₂ + trace CaO.MgO.2SiO₂	
30	9	61	1327	15	Glass + CaO.MgO.2SiO₂	
31	8·5	60·5	1327	25	Glass + CaO.MgO.2SiO₂	1, 3
31	9	60	1334	15	Glass + CaO.MgO.2SiO₂	
32	8	60	1344	30	Glass + αCaO.SiO₂	
			1340	20	Glass + 5CaO.2MgO.6SiO₂ + CaO.MgO.2SiO₂	
33	10	57	1350	20	Glass + 5CaO.2MgO.6SiO₂ + trace CaO.MgO.2SiO₂	
35	11	54	1355	25	Glass + 5CaO.2MgO.6SiO₂	
32	8	60	1344	30	Glass + αCaO.SiO₂	13, 14
			1340	180	Glass + 5CaO.2MgO.6SiO₂ + trace CaO.MgO.2SiO₂	
35	11	54	1355	25	Glass + 5CaO.2MgO.6SiO₂	
36	12	52	1368	25	Glass + αCaO.SiO₂	
32	7	61	1330-1335	240	Glass + trace SiO₂ + βCaO.SiO₂ + 5CaO.2MgO.6SiO₂	14, 16
30	20	50	1354	15	No glass + 2CaO.MgO.2SiO₂ + CaO.MgO.2SiO₂	3, 4
			1359	20	All glass	
32	18	50	1367	15	Glass + 2CaO.MgO.2SiO₂	
33	16·5	50·5	1366	20	Glass + trace 2CaO.MgO.2SiO₂	
34	15	51	1361	20	Glass + trace 2CaO.MgO.2SiO₂ + trace CaO.MgO.2SiO₂	
36	13	51	1352	15	Glass + trace 2CaO.MgO.2SiO₂	
23	22·5	54·5	1385	20	Glass + CaO.MgO.2SiO₂	4, 5
25	22	53	1388	20	Glass + 2MgO.SiO₂	
29	20	51	1367	15	Glass + CaO.MgO.2SiO₂	
29	21	50	1365	20	Glass + 2MgO.SiO₂ + trace CaO.MgO.2SiO₂	
37	12	51	1366	15	Glass + trace αCaO.SiO₂	13, 6
38	11	51	1366	25	Glass + trace αCaO.SiO₂	
38	12	50	1381	25	Glass + 2CaO.MgO.2SiO₂	
42·4	8·8	48·8	1403	15	Glass + αCaO.SiO₂	
44	8·5	47·5	1406	20	Glass + trace 2CaO.MgO.2SiO₂	
45	8	47	1409	15	Glass + αCaO.SiO₂	
47	7	46	1393	30	Glass + trace αCaO.SiO₂ + trace 2CaO.MgO.2SiO₂	
47	8	45	1390	15	Glass + 2CaOMgO.2SiO₂	
49	6	45	1379	20	Glass + αCaO.SiO₂ + trace · 2CaO.MgO.2SiO₂	
50	5	45	1380	60	Glass + 3CaO.2SiO₂	6, D
51·5	3·5	45	1417	10	Glass + trace αCaO.SiO₂ + trace 3CaO.2SiO₂	
50	6	44	1389	15	Glass + 2CaO.SiO₂	7, C
51	5	44	1410	15	Glass + 2CaO.SiO₂	

[36] The formulas of the pure compounds will be given to denote the phases, but in many cases the actual phases have not such compositions, being solid solutions and therefore variable in composition.

Composition wt. %			Temp.	Time in	Phases present[36]	Boundary
CaO	MgO	SiO₂	°C.	min.		
53	3	44	1450	30	Glass + 2CaO.SiO₂	7, C
49	7	44	1398	15	Glass + trace 2CaO.SiO₂ + trace 2CaO.MgO.2SiO₂	7, 8
47	9	44	1426	15	Glass + 2CaO.MgO.2SiO₂	
46	10	44	1410	60	Glass + 2CaO.MgO.2SiO₂	
45	12	43	1450	20	Glass + 2CaO.SiO₂	
42	15	43	1450	30	Glass + 2CaO.SiO₂	
42	14·5	43·5	1448	15	Glass + 2CaO.SiO₂ + 2CaO.MgO.2SiO₂	
			1453	20	Glass	
39	18	43	1444	20	Glass + 2CaO.MgO.2SiO₂	
39·5	18	42·5	1449	35	Glass + 2CaO.SiO₂	
36	20·5	43·5	1438	15	Glass + CaO.MgO.SiO₂ + 2CaO.MgO.2SiO₂	8, 9
			1445	20	Glass	
34	22	44	1445	30	Glass	
			1439	30	Glass + CaO.MgO.SiO₂ + 2CaO.MgO.2SiO₂	
35	22	43	1473	20	Glass + CaO.MgO.SiO₂	
31·5	22	46·5	1410	30	Glass + 2MgO.SiO₂	4, 9
33	22	45	1428	20	Glass + 2MgO.SiO₂ + 2CaO.MgO.2SiO₂	
			1432	15	Glass	
32	25	43	1477	15	Glass + 2MgO.SiO₂	9, 11
32	26	42	1501	60	Glass + 2MgO.SiO₂	
33	24	43	1472	15	Glass + CaO.MgO.SiO₂	
33	25	42	1460	30	Glass + CaO.MgO.SiO₂	
37	21	42	1467	15	Glass + CaO.MgO.SiO₂	8, 10
37	22	41	1485	15	Glass + CaO.MgO.SiO₂	
38	20	42	1483	15	Glass + CaO.MgO.SiO₂	
38	21	41	1489	15	Glass + CaO.MgO.SiO₂ + 2CaO.SiO₂	
			1493	15	Glass	
38	22	40	1506	15	Glass + 2CaO.SiO₂	
39	19	42	1484	15	Glass + 2CaO.SiO₂	
39	20	41	1492	15	Glass + 2CaO.SiO₂	
34	25	41	1507	20	Glass + MgO	10, 11
37	23	40	1517	20	Glass + MgO	
38	23	39	1539	10	Glass + MgO	10, 12
40	22	38	1560	30	Glass + MgO + trace 2CaO.SiO₂	
44	21	35	1690	30	Glass + trace MgO + trace 2CaO.SiO₂	
31·5	27	41·5	1522	15	Glass + MgO + 2MgO.SiO₂	12, H
30	28	42	1537	30	Glass + 2MgO.SiO₂	
29	30	41	1545	15	Glass + MgO	

The β2CaO.SiO₂ field, if such a field exists, is too small to be shown upon the diagram. If no solid solution exists, it consists of that portion of the 2CaO.SiO₂ field which lies below the isotherm[37] of 1420° since the inversion of the β form to the α form in the pure compound occurs at this temperature. The points 14 and 16 lie too close to the point 15 to be separately located.

[37] See figure 12, beyond.

The limits of the lime field were obtained by interpolation. One quench at 1660°C of a charge with a composition lime 55, magnesia 25, silica 20, showed no glass and in it crystals of $2CaO.SiO_2$ and lime could be identified. If an equilibrium condition had been reached this indicates a eutectic relation between lime, magnesia and $a2CaO.SiO_2$ and this we have assumed to be true in making our diagrams. However, Rankin and Wright found that, in the binary system, lime and silica first gave rise to $2CaO.SiO_2$ and lime before combining to give $3CaO.SiO_2$, and a similar condition may have been encountered by us. If a eutectic exists (as we have assumed to be the case) the temperature of it must lie above 1900°C, the decomposition temperature of $3CaO.SiO_2$.

The heat treatment of charges in which the compound $2CaO.MgO.2SiO_2$ occurs as a primary or a secondary phase, as given in Table I, may seem to be far too short a time in view of the tendency shown by solutions of this compound to undercool. Such is, however, not the case, since if care be taken to start with fully crystallized material, and the temperature of the charge be never allowed to exceed the desired temperature, this difficulty can be and was avoided. In studies of this nature the length of the heat treatment of itself means but little unless the properties of the reacting phases are known and these may be of such a character as to necessitate a knowledge of the original state and previous history of each charge before one can judge if the heat treatment has been sufficient. The experiments carried out at temperatures above 1600°C were made in the cascade furnace[38] designed for the determination of the melting point of cristobalite.

TEMPERATURE RELATIONS ALONG THE BOUNDARY LINES EXCLUSIVE OF QUINTUPLE POINTS.

The temperatures at which the complete fusion of the charges with compositions represented by the boundary lines takes place, may be determined either directly upon such charges, or indirectly by following the crystallization curves of the compositions which lie within the adjacent fields. This latter method offers no especial

[38] J. B. Ferguson and H. E. Merwin, this Journal, **46**, 417, 1918.

difficulty if solid solutions do not exist and the crystallization lines are straight lines, but if solid solutions exist these lines which represent the changes in the composition of the liquid in a charge during crystallization are curved, and since their curvature is often difficult to determine, in this case the method may be quite uncertain. In the ternary system under investigation there is much solid solution and for this reason most of the charges which were used for this part of the study lay close to the boundary lines in composition. The experimental results of this study are given in Table II.

TABLE II.

Quenches which determine the melting temperatures along the boundary lines.

Composition wt. %			Temp. °C.	Time in min.	Phases present	Boundary
CaO	MgO	SiO₂				
32	6	62	1361	15	Glass + αCaO.SiO₂ + SiO₂	1, 16, 15, E
			1370	15	Glass + αCaO.SiO₂	
			1339	15	Glass + αCaO.SiO₂ + SiO₂	
			1334	20	Glass + βCaO.SiO₂ + SiO₂	
32	7	61	1331	20	Glass + βCaO.SiO₂ + SiO₂	
			1337	20	Glass + αCaO.SiO₂	
31	7	62	1343	20	Glass + SiO₂	
			1338	20	Glass + SiO₂ + αCaO.SiO₂	
23	14.5	62.5	1370	20	Glass + trace SiO₂	1, 2
			1365	25	Glass + trace SiO₂ + CaO.MgO.2SiO₂	
25.25	12.5	62.5	1352	20	Glass + CaO.MgO.SiO₂	
			1350	20	Glass + CaO.MgO.2SiO₂ + SiO₂	
28	10	62	1349	30	Glass	
			1338	20	Glass + SiO₂ + CaO.MgO.2SiO₂	
31	9	60	1326	15	Glass + CaO.MgO.2SiO₂	1, 3
			1321	15	Glass + CaO.MgO.2SiO₂ + 5CaO.2MgO.6SiO₂	
32	8	60	1340	20	Glass + trace CaO.MgO.2SiO₂ + trace 5CaO.2MgO.6SiO₂	
33	10	57	1352	30	Glass	
			1350	20	Glass + 5CaO. 2MgO.6SiO₂ + CaO.MgO.2SiO₂	
35	11	54	1353	20	Glass + 5CaO.2MgO.6SiO₂ + CaO.MgO.2SiO₂	
			1356	25	Glass + 5CaO.2MgO.6SiO₂	
38	11	51	1361	30	Glass + (trace αCaO.SiO₂)* + 5CaO.2MgO.6SiO₂ + trace CaO.MgO.2SiO₂	1, 3
36	12	52	1368	25	Glass + αCaO.SiO₂	13, 14, 15
			1363	25	Glass + αCaO.SiO₂ + 5CaO.2MgO.6SiO₂	
32	8	60	1344		Glass + αCaO.SiO₂	
36	12	52	1368		Glass + αCaO.SiO₂	

(See also quenches 1, 3 above)

* αCaO.SiO₂ is here unstable.

Am. Jour. Sci.—Fourth Series, Vol. XLVIII, No. 284.—August, 1919.

7

Composition wt. %			Temp. °C.	Time in min.	Phases present	Boundary
CaO	MgO	SiO₂				
32	18	50	1365	20	Glass + CaO.MgO.2SiO₂ + 2CaO.MgO.2SiO₂	3, 4
			1371	20	Glass + 2CaO.MgO.2SiO₂	
33	16·5	50·5	1367	20	Glass + 2CaO.MgO.2SiO₂	
			1364	20	Glass + 2CaO.MgO.2SiO₂ + CaO.MgO.2SiO₂	
34	15	51	1361	20	Glass + trace 2CaO.MgO.2SiO₂ + trace CaO.MgO.2SiO₂	
23	22·5	54·5	1383	20	Glass + CaO.MgO.2SiO₂	4, 5
			1379	20	No glass	
25	22	53	1383	20	Glass + trace CaO.MgO.2SiO₂ + 2MgO.SiO₂	
			1388	20	Glass + 2MgO.SiO₂	
26	23	51	1375	20	Glass + 2MgO.SiO₂ + CaO.MgO.2SiO₂	
			1380	20	Glass + 2MgO.SiO₂	
29	21	50	1365	20	Glass + 2MgO.SiO₂ + trace CaO.MgO.2SiO₂	
50	5	45	1384	20	Glass + 3CaO.2SiO₂	6, D
			1378	20	Glass + 3CaO.2SiO₂ + αCaO.SiO₂	
51·5	3·5	45	1410	10	Glass + αCaO.SiO₂ + 3CaO.2SiO₂	
			1417	10	Glass + trace crystals	
51	5	44	1404	15	Glass + 2CaO.SiO₂ + 3CaO.2SiO₂	7, C
			1410	15	Glass + 2CaO.SiO₂	
53	3	44	1430	15	Glass + 2CaO.SiO₂ + trace 3CaO.2SiO₂	
37	12	51	1367	15	Glass + αCaO.SiO₂	3, 13, 6
			1362	15	Glass + αCaO.SiO₂ + 2CaO.MgO.2SiO₂	
38	12	50	1375	25	Glass + αCaO.SiO₂ + 2CaO.MgO.2SiO₂	
			1381	25	Glass + 2CaO.MgO.2SiO₂	
42·4	8·8	48·8	1403	15	Glass + αCaO.SiO₂	
			1398	15	Glass + αCaO.SiO₂ + 2CaO.MgO.2SiO₂	
44	8·5	47·5	1402	20	Glass + αCaO.SiO₂ + 2CaO.MgO.2SiO₂	
			1406	20	Glass + 2CaO.MgO.2SiO₂	
45	8	47	1409	15	Glass + αCaO.SiO₂	
			1403	15	Glass + αCaO.SiO₂ + 2CaO.MgO.2SiO₂	
47	7	46	1393	30	Glass + trace αCaO.SiO₂ + trace 2CaO.MgO.2SiO₂	
49	7	44	1405	15	Glass + 2CaO.SiO₂ + 2CaO.MgO.2SiO₂	7, 8
			1410	15	Glass	
47	9	44	1422	15	Glass + 2CaO.SiO₂ + trace 2CaO.MgO.2SiO₂	
45	12	43	1440	20	Glass + 2CaO.SiO₂	
			1432	15	Glass + 2CaO.SiO₂ + 2CaO.MgO.2SiO₂	
42	14·5	43·5	1448	15	Glass + 2CaO.SiO₂ + 2CaO.MgO.2SiO₂	
			1453	15	Glass	
36	20·5	43·5	1445	20	Glass	8, 9
			1438	15	Glass + 2CaO.MgO.2SiO₂ + CaO.MgO.SiO₂	

Composition wt. %			Temp. °C.	Time in min.	Phases present	Boundary
CaO	MgO	SiO$_2$				
34	22	44	1445	30	Glass	8, 9
			1442	30	Glass + 2CaO.MgO.2SiO$_2$ + CaO.MgO.SiO$_2$	
39	18	43	1444	20	Glass + 2CaO.MgO.2SiO$_2$	
			1429	90	No 2CaO.SiO$_2$	
38	20	42	1436	20	No 2CaO.SiO$_2$	
33	22	45	1432	20	Glass	4, 9
			1428	15	Glass + 2MgO.SiO$_2$ + 2CaO.MgO.2SiO$_2$	
32	23	45	1430	20	Glass + 2MgO.SiO$_2$	
			1423	15	Glass + 2MgO.SiO$_2$ + 2CaO.MgO.2SiO$_2$	
31·5	22	46·5	1410	30	Glass + 2MgO.SiO$_2$	
			1406	25	Glass + 2MgO.SiO$_2$ + 2CaO.MgO.2SiO$_2$	
30	22	48	1415	20	Glass + 2MgO.SiO$_2$	
			1392	30	Glass + 2MgO.SiO$_2$ + trace 2CaO.MgO.2SiO$_2$	
34	25	41	1502	30	Glass + MgO + CaO.MgO.SiO$_2$	10, 11
			1510	20	Glass + MgO	
35	25	40	1511	15	Glass + MgO + CaO.MgO.SiO$_2$	
			1516	15	Glass + MgO	
38	21	41	1489	15	Glass + 2CaO.SiO$_2$ + CaO.MgO.SiO$_2$	8, 10
			1493	15	Glass	
40	22	38	1537	30	Glass + MgO + trace 2CaO.SiO$_2$	10, 12
44	21	35	1660	15	Glass + MgO + 2CaO.SiO$_2$	
			1690	30	Glass + trace MgO + trace 2CaO.SiO$_2$	
31·5	27	41·5	1529	20	Glass	11, H
			1522	15	Glass + MgO + 2MgO.SiO$_2$	

The similarity between the optical properties of the monticellite crystals which contain in solution some forsterite and the forsterite crystals themselves is very marked, and for this reason the melting temperatures along the boundary line 9,11 in fig. 8 could not be determined except by the slope of the liquidus of the adjacent fields.

THE QUINTUPLE POINTS.

Fourteen quintuple or invariant points at which three crystalline phases and a liquid can co-exist are to be found in this ternary system, and of these, six are true eutectics. These quintuple points are the points of intersection of three boundary lines and when the temperatures along each of three lines fall as they approach the point of intersection the point is called a eutectic.

Point 1, fig. 8, is a eutectic between diopside, tridy-

mite, and $5CaO.2MgO.6SiO_2$. It has a composition
CaO 30·6, MgO 8, SiO$_2$ 61·4, and a temperature
$1320 \pm 5°C$.

TABLE III.

Quenches which determine the temperature relations at point 1.

Composition wt. %			Temp. °C.	Time in min.	Phases present
CaO	MgO	SiO$_2$			
31	7	62	1324	20	Glass + crystals
			1319	45	No glass
31	9	60	1321	15	Glass + crystals
			1316	15	No glass
32	7	61	1319	20	No glass
			1324	25	Glass + crystals
32	8	60	1315	20	No glass
			1320	20	Glass + crystals

Point 16 is a non-eutectic at which tridymite, a wollas-
tonite solid solution, and a $5CaO.2MgO.6SiO_2$ solid solu-
tion can co-exist with a liquid. The temperature and
location of this point have not been separately deter-
mined. It lies very close to point 15 with a probable
temperature of $1330 \pm 5°C$.

Point 15 is a non-eutectic between pseudowollastonite,
a wollastonite solid solution and tridymite. It occurs
at the composition CaO 31·3, MgO 7·2, SiO$_2$ 61·5, and its
temperature is $1335 \pm 5°C$.

TABLE IV.

Quenches which determine the temperature relations at point 15.

Composition wt. %			Temp. °C.	Time in min.	Phases present
CaO	MgO	SiO$_2$			
31	7	62	1343	20	Glass + SiO$_2$
			1338	20	Glass + SiO$_2$ + αCaO.SiO$_2$
32	6	62	1339	20	Glass + SiO$_2$ + αCaO.SiO$_2$
			1334	20	Glass + SiO$_2$ + (βCaO.SiO$_2$ or 5CaO.2MgO.6SiO$_2$)
32	7	61	1331	20	Glass + SiO$_2$ + (βCaO.SiO$_2$ or 5CaO.2MgO.6SiO$_2$)
			1337	20	Glass + αCaO.SiO$_2$

Point 14[39] is a quintuple point between pseudowollas-
tonite, a wollastonite solid solution, and a $5CaO.2MgO.$
$6SiO_2$ solid solution. It has a composition CaO 31·4,
MgO 7·6, SiO$_2$ 61, and a temperature of $1340 \pm 5°C$.

Point 13 is a quintuple point between pseudowollaston-

[39] The location and temperatures of points 14 and 13 will be discussed
under the wollastonite and 5CaO.2MgO.6SiO$_2$ solid solutions.

ite, $5CaO.2MgO.6SiO_2$, and $2CaO.MgO.2SiO_2$. The composition is CaO 36·7, MgO 12·3, SiO_2 51, and the temperature $1365 \pm 5°C$.

TABLE V.

Quenches which indicate the temperature relations at point 13.

Composition wt. %			Temp.	Time in	Phases present
CaO	MgO	SiO₂	°C.	min.	
36	12	52	1368	25	Glass + $\alpha CaO.SiO_2$
			1363	25	Glass + $\alpha CaO.SiO_2$ + $5CaO.2MgO.6SiO_2$
38	11	51	1366	25	Glass + $\alpha CaO.SiO_2$ + $5CaO.2MgO.6SiO_2$
37	12	51	1366	15	Glass + $\alpha CaO.SiO_2$
38	12	50	1375	27	Glass + $\alpha CaO.SiO_2$ + $2CaO.MgO.2SiO_2$

Point 3 is a eutectic between $\alpha 5CaO.2MgO.6SiO_2$ solid solution, diopside and $2CaO.MgO.2SiO_2$. Its composition is CaO 36, MgO 12·6, SiO_2 51·4, and its temperature $1350 \pm 5°C$.

TABLE VI.

Quenches which determine the temperature relations at point 3.

Composition wt. %			Temp.	Time in	Phases present
CaO	MgO	SiO₂	°C.	min.	
36	13	51	1345	30	No glass
			1350	30	Glass + $5CaO.2MgO.6SiO_2$ + $CaO.MgO.2SiO_2$ + $2CaO.MgO.2SiO_2$
			1354	120	Glass + crystals
			1348	120	Crystals + merest trace if any of glass
37	12	51	1351	20	All crystals
			1353	30	Glass + crystals

Point 4 is a eutectic between $2CaO.MgO.2SiO_2$, forsterite and diopside. The composition is CaO 29·8, MgO 20·2, SiO_2 50, and the temperature $1357 \pm 5°C$.

TABLE VII.

Quenches which determine the temperature relations at point 4.

Composition wt. %			Temp.	Time in	Phases present
CaO	MgO	SiO₂	°C.	min.	
29	21	50	1354	30	No glass
			1359	20	Glass + crystals
30	20	50	1354	15	No glass
			1359	20	All glass

Point 6 is a eutectic between pseudowollastonite, $3CaO.2SiO_2$ and $2CaO.MgO.2SiO_2$. Its composition is CaO 49·2, MgO 6·3, SiO_2 44·5, and its temperature $1377 \pm 5°C$.

TABLE VIII.

Quenches which determine the temperature relations at point 6.

| Composition wt. % | | | Temp. | Time in | Phases present |
CaO	MgO	SiO₂	°C.	min.	
49	6	45	1374	20	No glass
			1379	20	Glass + crystals
50	5	45	1378	20	Glass + crystals
			1374	20	No glass
49	7	44	1375	15	No glass
			1384	15	Glass + crystals

Point 7 is a quintuple point between $\beta 2CaO.SiO_2$, $3CaO.$ $2SiO_2$ and $2CaO.MgO.2SiO_2$. The composition is CaO 49·5, MgO 6·2, SiO₂ 44·3, and the temperature is $1387 \pm 5°C$.

TABLE IX.

Quenches which determine the temperature relations at point 7.

| Composition wt. % | | | Temp. | Time in | Phases present |
CaO	MgO	SiO₂	°C.	min.	
49	7	44	1384	15	Glass + $3CaO.2SiO_2$ + $2CaO.MgO.2SiO_2$
			1389	15	Glass + $2CaO.SiO_2$ + $2CaO.MgO.2SiO_2$
50	6	44	1391	15	Glass + $2CaO.SiO_2$ + $3CaO.2SiO_2$
			1384	15	Glass + $2CaO.MgO.2SiO_2$ + $3CaO.2SiO_2$

Point 8 is a eutectic between $2CaO.MgO.2SiO_2$, $a2CaO.$ SiO_2 and a monticellite solid solution. Its composition is CaO 39, MgO 18·3, SiO₂ 42·7, and its temperature $1436 \pm 5°C$.

TABLE X.

Quenches which determine the temperature relations at point 8.

| Composition wt. % | | | Temp. | Time in | Phases present |
CaO	MgO	SiO₂	°C.	min.	
39	19	42	1443	20	Glass + crystals
			1436	20	No glass
			1443	60	Glass + crystals
			1438	45	No glass, crystals including $2CaO.SiO_2$
39·5	18	42·5	1443	30	Glass + crystals
			1438	20	Glass + crystals
			1432	15	No glass, crystals including $2CaO.SiO_2$

Point 9 is a quintuple point between $2CaO.MgO.2SiO_2$, forsterite, and a monticellite solid solution. Its composition is CaO 33·3, MgO 22·3, SiO₂ 44·4, and its temperature $1436 \pm 5°C$.

TABLE XI.

Quenches which determine the temperature relations at point 9.

| Composition wt. % | | | Temp. | Time in | Phases present |
CaO	MgO	SiO$_2$	°C.	min.	
33	24	43	1439	20	Glass + 2MgO.SiO$_2$ + CaO.MgO.SiO$_2$ + No 2CaO.MgO.2SiO$_2$
			1434	20	Glass + 2CaO.MgO.2SiO$_2$ + 2MgO.SiO$_2$
34	22	44	1439	30	Glass + 2CaO.MgO.2SiO$_2$ + CaO.MgO.SiO$_2$
			1434	35	Glass + 2CaO.MgO.2SiO$_2$ + 2MgO.SiO$_2$

Point 10 is a quintuple point between periclase, a monticellite solid solution and a2CaO.SiO$_2$. It has a composition CaO 37·3, MgO 22·3, SiO$_2$ 40·3, and a temperature 1498 ± 5°C.

TABLE XII.

Quenches which determine the temperature relations at point 10

| Composition wt. % | | | Temp. | Time in | Phases present |
CaO	MgO	SiO$_2$	°C.	min.	
37	23	40	1494	20	Glass + 2CaO.SiO$_2$ + CaO.MgO.SiO$_2$
			1500	25	Glass + trace MgO + CaO.MgO.SiO$_2$
38	22	40	1503	10	Glass + MgO + 2CaO.SiO$_2$
			1498	20	Glass + 2CaO.SiO$_2$ + CaO.MgO.SiO$_2$

Point 11 is a quintuple point between periclase, forsterite and a monticellite solid solution. Its composition is CaO 32·1, MgO 26·4, SiO$_2$ 41·5, and its temperature 1502 ± 5°C.

TABLE XIII.

Quenches which determine the temperature relations at point 11.

| Composition wt. % | | | Temp. | Time in | Phases present |
CaO	MgO	SiO$_2$	°C.	min.	
31·5	27	41·5	1499	25	Glass + 2MgO.SiO$_2$ + CaO.MgO.SiO$_2$ + No MgO
			1507	25	Glass + MgO + 2MgO.SiO$_2$
32	26	42	1496	15	Glass + 2MgO.SiO$_2$ + CaO.MgO.SiO$_2$
30	28	42	1500	25	No MgO + ?
			1508	15	MgO + ?

Point 12 is a eutectic[40] between periclase, lime and a2CaO.SiO$_2$. Its composition and temperature are uncertain since the latter lies above the working temperatures of either of our furnaces and the rapidity with which a2CaO.SiO$_2$ and periclase both crystallize precluded the

[40] See the discussion of the lime field following Table I.

use of the iridium furnace, but the temperature probably lies above 1900°C, the temperature at which the tricalcium silicate decomposes into lime and $a2CaO.SiO_2$.

The exact temperature relations at the quintuple points, at the quadruple points on the side lines, and along the boundary lines, may be depicted by constructing a model which has as a base the concentration diagram, fig. 8, and upon which the temperatures are shown as vertical dis-

Fig. 9.
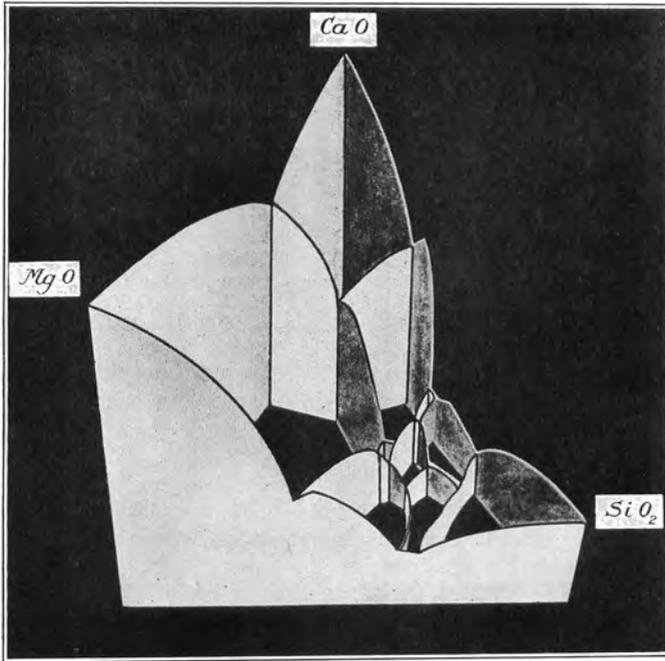
Fig. 9.—A model constructed by plotting vertically upon the concentration diagram as given in fig. 8, the temperature of complete fusion of the compositions lying along the boundaries of the fields of stability of the various phases.

tances above this base. Fig. 9 is a photograph of such a model.[41] This particular model includes and correlates the previous results of Bowen on this ternary system,

[41] This is the framework of a solid model. A description of the constructional details of such a model is given by Rankin and Wright, this Journal, **39**, 1, 1915.

Fig. 10a.
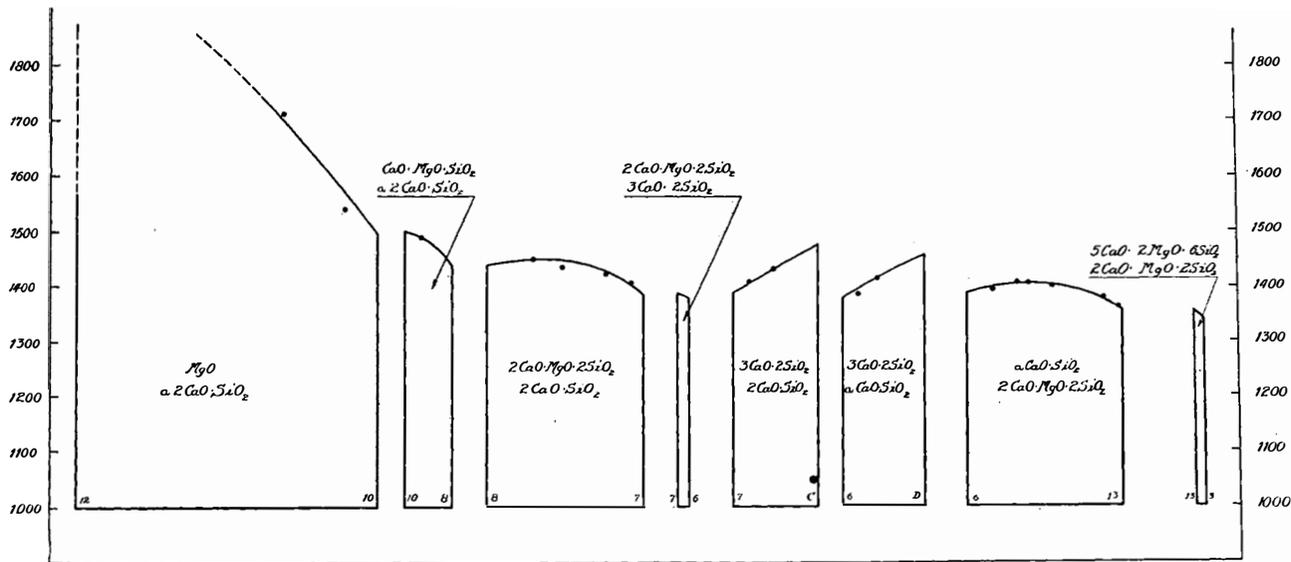
Fig. 10a.—The vertical projections of the boundary lines shown in fig. 9 which indicate the temperature relations along these lines.

FIG. 10*b*.
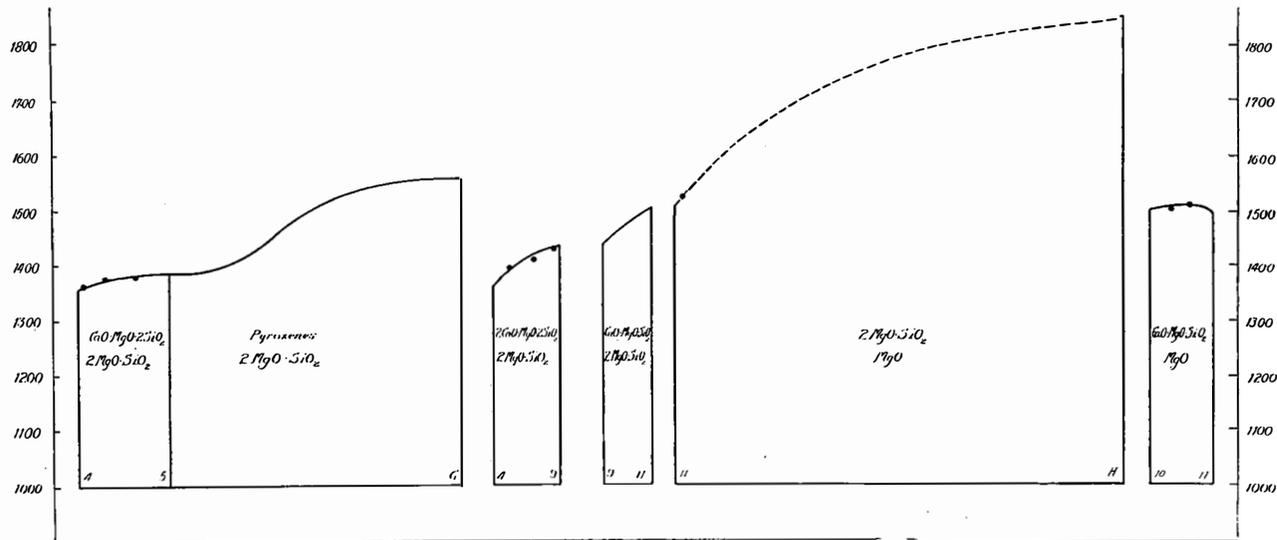
FIG. 10*b*.—The vertical projections of the boundary lines shown in fig. 9 which indicate the temperature relations along these lines.
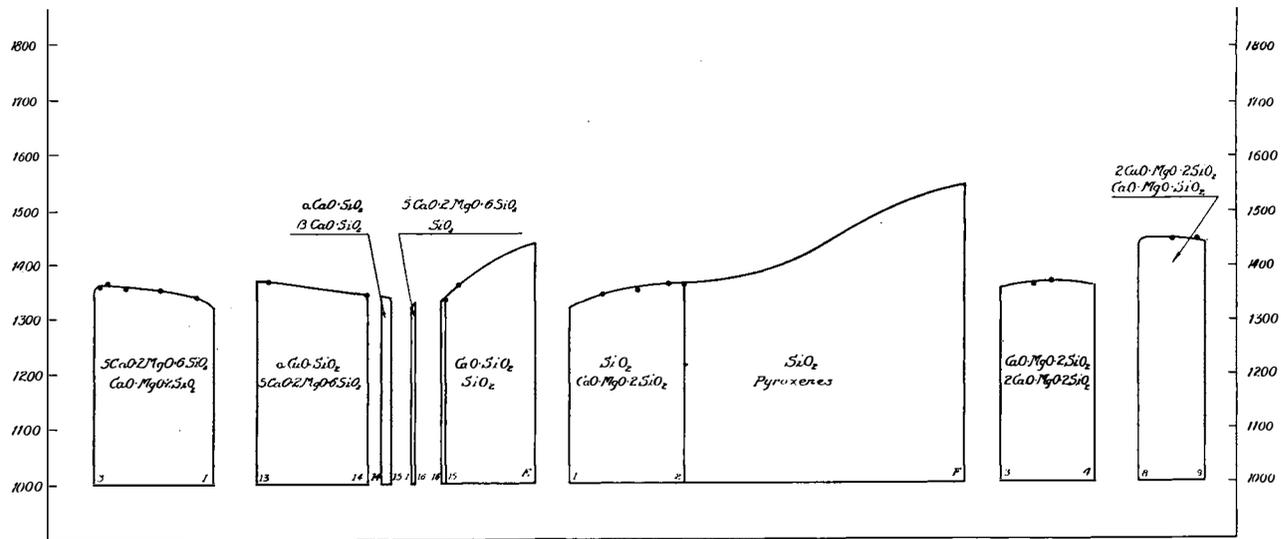
FIG. 10c.—The vertical projections of the boundary lines shown in fig. 9 which indicate the temperature relations along these lines.

with our results given in Tables II–XIII, inclusive, in addition to the results of the various investigators on the side-line binary systems. A vertical projection of

FIG. 11.

FIG. 11.—The complete temperature concentration diagram which was constructed by plotting vertically upon the concentration diagram given in fig. 8 the temperatures of complete fusion of the various compositions.

each of the lines within the ternary system is given in figs. 10 (a, b and c), and perhaps shows these relations more clearly than does the model itself.

These curves are also of interest because they serve as

a check upon the experimental methods employed. The curves 1F and 4G are perhaps the best illustrations of what reliance may be placed upon the methods. Each of these curves represents the work of several investi-
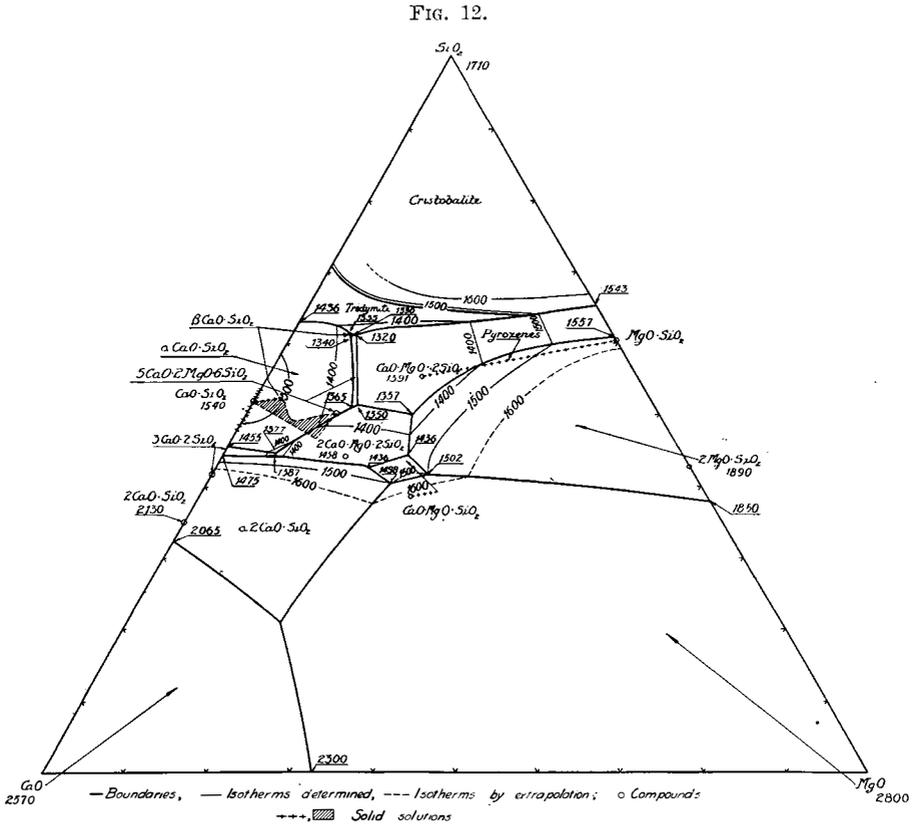
FIG. 12.

FIG. 12.—A concentration diagram somewhat similar to that given in fig. 8 upon which the isotherms showing the temperatures of complete melting of the various compositions are drawn. The diagram is on a wt. per cent basis.

gators; 2, F, and 5, G were determined by N. L. Bowen, 1, 2, and 4, 5, by ourselves. The agreement here obtained is of the order usually found between experiments of the same series, but in this case somewhat exceeds that usually obtained by us when the identical apparatus was not used for all experiments. A somewhat similar

agreement was found between the concentration relations, and this fact may readily be gleaned from an inspection of figs. 6 and 8.

A maximum is shown on the line 8, 9, although it has not been experimentally determined, the line 8, 9 being

FIG. 13.

FIG. 13.—A similar diagram to that shown in 12 except that it is on a mol. per cent basis. With this exception this paper has been written upon a wt. per cent basis.

too flat. The reasons for placing a maximum here will be discussed under the monticellite solid solutions, and similarly the peculiar relations exhibited by the lines 1, 3 and 13, 14, 15 will be discussed under the wollastonite solutions.

THE MELTING TEMPERATURES WITHIN THE FIELDS.

The temperatures at which charges with compositions lying within the fields become completely fused are given in Tables XIV–XXI, inclusive.

TABLE XIV.

Melting temperatures in the silica field: Melting point of cristobalite 1710 ± 10°C.

Composition wt. %			Temp. °C.	Time in min.	Phases present
CaO	MgO	SiO₂			
23	7	70	1675	120	Glass
previous charge reheated			1638	30	Glass + crystals
23	14·5	62·5	1375	20	Glass + trace crystals
25	10	65	1485	45	Glass
			1472	15	Glass + trace crystals
26	7	67	1546	10	Glass
			1536	10	Glass + crystals
30	5	65	1463	15	Glass + crystals
			1472	10	Glass
31	7	62	1347	20	Glass
			1343	20	Glass + trace crystals

TABLE XV.

Melting temperatures in the diopside field; melting point of diopside 1391°C.

Composition wt. %			Temp. °C.	Time in min.	Phases present
CaO	MgO	SiO₂			
28	13	59	1375	10	Glass
			1370	10	Glass + crystals
30	15	55	1375	15	Glass + crystals
			1381	10	Glass

The melting temperatures of compositions lying within the fields of the βCaO.SiO₂ or wollastonite solid solutions and the 5CaO.2MgO.6SiO₂ solid solutions must be obtained from the temperatures of the boundaries, as the fields are too narrow to warrant an investigation.

TABLE XVI.

Melting temperatures in the $_{\alpha}$CaO.SiO₂ field; melting point of $_{\alpha}$CaO.SiO₂ 1540°C.

Composition wt. %			Temp. °C.	Time in min.	Phases present
CaO	MgO	SiO₂			
32	6	62	1370	15	Glass + trace crystals
35	5	60	1402	10	Glass
			1395	10	Glass + crystals
40	5	55	1468	10	Glass + trace crystals

Composition wt. %			Temp. °C.	Time in min.	Phases present
CaO	MgO	SiO₂			
45	5	50	1476	10	Glass
			1468	15	Glass + crystals
46·7	3·1	50·2	1490	15	Crystals + trace glass?
			1500	15	Glass
44·3	2·8	52·4	1500	15	Trace glass + crystals
			1510	15	Glass + trace crystals
44	6	50	1470	15	Glass + trace crysals

TABLE XVII.

Melting temperatures in the 2CaO.MgO.2SiO₂ field; melting point of
2CaO.MgO.2SiO₂ 1458 ± 5°C.

Composition wt. %			Temp. °C.	Time in min.	Phases present
CaO	MgO	SiO₂			
35	20	45	1446	10	Glass
			1440	10	Glass + crystals
39	14	47	1431	20	Glass + trace crystals
39	15·5	45·5	1440	10	Glass + crystals .
			1445	10	Glass
39	17	44	1449	20	Glass + crystals
			1454	20	Glass
39	18	43	1450	20	Glass
			1444	20	Glass + crystals
40·33	14·66	45	1455	5	Glass
			1450	10	Glass + crystals
41	13	46	1434	20	Glass
			1430	20	Glass + crystals
			1459	20	Glass
41	15	44	1456	15	Crystals only
	2CaO.MgO.2SiO₂		1460	10	Glass
			1455	10	Crystals only

The phase 3CaO.2SiO₂ is unstable at its melting point
and its field is too small to warrant the determination of
melting temperatures within it, other than by interpola-
tion from the boundaries.

The phase α2CaO.SiO₂ melts at 2130 ± 10°C and the
temperature gradient within its field is so steep that but
few melting temperatures were determined.

TABLE XVIII.

Melting temperatures within the 2CaO.SiO₂ field. Melting point of
α2CaO.SiO₂ 2130 ± 10°C.

Composition wt. %			Temp. °C.	Time in min.	Phases present
CaO	MgO	SiO₂			
48	10	42	1547	10	Glass + trace crystals
45	12	43	1470	15	Glass + crystals
			1475	15	Glass
40	20	40	1546	10	Glass
			1536	10	Glass + crystals

The phase CaO.MgO.SiO$_2$ is unstable at its melting point and in addition is variable in composition since it belongs to a series of solid solutions of forsterite in pure monticellite.

TABLE XIX.

Melting temperatures within the monticellite field.

Composition wt. %			Temp. °C.	Time in min.	Phases present
CaO	MgO	SiO$_2$			
33	25	42	1502	16	Glass + crystals
			1509	16	Glass
35	22	43	1478	15	Glass
			1473	15	Glass + crystals
37	21	42	1483	15	Glass
			1467	15	Glass + crystals
37	22	41	1497	15	Glass
			1487	15	Glass + crystals
38	20	42	1489	18	Glass
			1483	15	Glass + crystals

TABLE XX.

Melting temperatures within the periclase field, the melting point of periclase 2800 ± 20°C.

Composition wt. %			Temp. °C.	Time in min.	Phases present
CaO	MgO	SiO$_2$			
34	25	41	1515	20	Glass + trace MgO
35	25	40	1539	10	Glass
			1528	10	Glass + crystals
37	23	40	1521	20	Glass
			1517	20	Glass + crystals

TABLE XXI.

Melting temperatures within the forsterite field, the melting point of forsterite 1890°C.

Composition wt. %			Temp. °C.	Time in min.	Phase presented
CaO	MgO	SiO$_2$			
24	24	52	1432	10	Glass
			1426	10	Glass + trace crystals
23	28	49	1528	10	Glass + trace crystals
27	26	47	1501	15	Glass + crystals
			1509	15	Glass
28	24	48	1460	10	Glass + crystals
			1468	10	Glass
30	25	45	1490	15	Glass
			1485	15	Glass + crystals
32	23	45	1459	15	Glass
			1445	20	Glass + crystals
32	25	43	1498	15	Glass + trace crystals
32	26	42	1506	20	Glass + crystals
			1510	20	Glass

The liquidus-solidus temperature relations have now, as far as possible, been determined over the entire ternary system and they may be represented by a solid model constructed by properly filling in the model shown in fig. 9. A photograph of this solid model is shown in fig. 11. These relations may also be indicated by means of a triangular concentration diagram similar to the one shown in fig. 8, upon which isotherms have been drawn and the temperature of the fixed points given. In figs. 12 and 13 are such diagrams, 12 given in weight percent and 13 in mol percent.

DISCUSSION OF THE FIELDS.

A complete discussion of the wollastonite, of the pseudowollastonite and of the $5CaO.2MgO.6SiO_2$ solid solutions and their respective fields will appear in a subsequent paper. The general conclusions only will be indicated at this time.

The pseudowollastonite field.—This field belongs to solid solutions whose compositions form an area bounded by the $CaO.SiO_2$-CaO side line, the $CaO.SiO_2$-diopside line and a line extending from the compositions CaO 44·4, MgO 3·1, SiO_2 52·5, on the $CaO.SiO_2$-diopside line to the composition CaO 46·7, MgO 3·5, SiO_2 49·8, on the $CaO.SiO_2$-$2CaO.MgO.2SiO_2$ line and probably to the composition CaO 50, SiO_2 50 on the side line.

The wollastonite field.—The evidence does no more than establish the existence of this tiny field which belongs to the most concentrated solid solution of diopside in wollastonite which decomposes at the highest temperature. This solid solution containing between 3·1 and 3·5 percent MgO or approximately 17 percent of diopside has the highest decomposition temperature, $1340 \pm 5°C$, the pure wollastonite inverting to pseudowollastonite at $1200°C$. The limit of 3·1 to 3·5 percent MgO agrees with the limit of 3·15 MgO (17 percent diopside) found by Allen and White as does the decomposition temperature of $1340°C$ with their observations.[42]

The $5CaO.2MgO.6SiO_2$ field.—This field belongs to a series of solid solutions which are not stable at their melting points and which lie on or near the $5CaO.2MgO.6SiO_2$ composition. The fact that the decomposition temperatures of these and other solid solutions rise sharply as

[42] This Journal, 27, 1, 1909.

the composition $5CaO.2MgO.6SiO_2$ is reached was interpreted as indicating the existence of this compound. Its decomposition temperature is somewhat difficult to determine directly but from the liquidus relations must be $1365 \pm 5°C$, the temperature which corresponds to point 13.

The diopside ($CaO.MgO.2SiO_2$) solid solution.—Diopside has previously been shown by several investigators to form no solid solution with silica, forsterite or pseudowollastonite. Similarly it does not form solid solutions with the compound $2CaO.MgO.2SiO_2$ to any great extent. A charge of the composition CaO 26·5, MgO 18·5, SiO_2 55, was found to contain after a 15 hour heat treatment at 1300°C, crystals of $2CaO.MgO.2SiO_2$ in such quantities as to indicate not more than a trace of such solid solutions. However, diopside forms a continuous series of solid solutions with clino-enstatite $MgO.SiO_2$, a thorough discussion of which has been given by Bowen.

The $CaO.MgO.SiO_2$ (monticellite) solid solutions.—The temperature relations along the monticellite-periclase boundary line 10, 11, are such as to indicate considerable solid solution between monticellite and forsterite.[43] The limit thus indicated would be about ten percent forsterite, or to the composition CaO 32, MgO 28·75, SiO_2 39·25. Owing to the difficulties encountered here, due to the great readiness with which magnesia crystallizes and the great slowness with which it is resorbed, only a few confirmatory experiments were made. These indicated that the solid solution extends at least to the composition CaO 33, MgO 28, SiO_2 39.

Attempts to prepare pure monticellite did not succeed. Instead of a homogeneous mass of this composition a mixture of crystals of $a2CaO.SiO_2$ and crystals of a monticellite solid solution was always obtained even though the original charge consisted of a glass in which very minute crystals of magnesia were imbedded. This result may be explained by reference to fig. 14 which is an enlargement of this portion of the diagram given in fig. 8. The arrows indicate the direction of falling temperatures. The maximum C on the line 10, 11, represents the decomposition temperature of the solid solution D and there

[43] The existence of such solutions was previously discovered but the somewhat crude apparatus used in the investigation made the interpretation of the results an uncertain matter. P. Herman, Zeit., d. deutsch Geol. Ges. 58, 39, 1906.

must be a maximum on the line 8, 9, at B although due to the slight temperature gradient we have been unable to detect it. The field B, 9, 11, C is the field of the solid solution D and the field B, 8, 10, C is the field of the solid solutions with compositions on the line DM. The exact liquidus-solidus relations cannot be determined because of the difficulties inherent in the microscopic examination of these solutions. The decomposition temperatures along DM are evidently all lower than the temperature at D but one cannot say if they change gradually from D to M or if they pass through a minimum between D and M. If a minimum is present then the point 10 represents a glass which can coexist with a solid solution of an
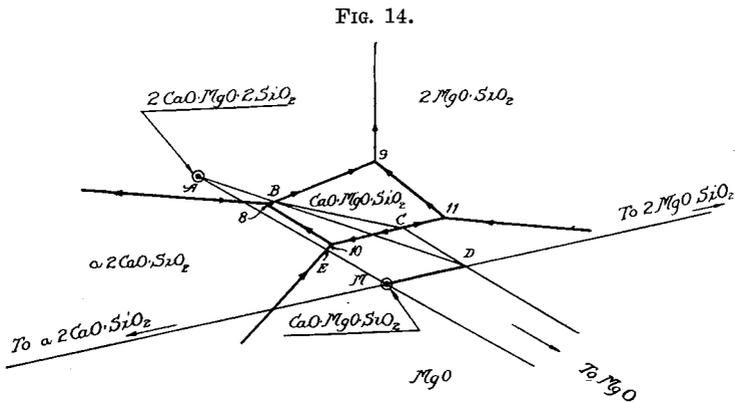
FIG. 14.

FIG. 14.—An enlargement of that part of the diagram given in fig. 8 which deals with the monticellite solid solutions with some additions designed to aid in the discussion of these solid solutions.

intermediate composition to D and M. If a minimum is not present this may or may not be the case and the pure compound may be stable in the presence of the glass 10. Our inability to prepare the pure compound cannot be reconciled to this latter theoretical possibility and it would therefore appear reasonably certain that the glass 10 corresponds to a solid solution with a composition intermediate with D and M. The crystallization of a glass M of the composition $CaO.MgO.SiO_2$ would be:

1. Liquid.
2. Magnesia and liquid. The liquid composition varies from M to E along ME.
3. Magnesia, $a2CaO.SiO_2$ and liquid. The liquid composition follows the line E 10 to 10.

4. The magnesia disappears and the charge becomes completely crystalline at 10 to form a mixture of α2CaO.SiO$_2$ and a solid solution X. The last liquid has a composition represented by the point 10. The solid solution X lies on the line MD between M and D.

Were it possible to make a reaction take place in the solid state in a reasonable time, pure monticellite would be formed when the mixture of α2CaO.SiO$_2$ and the solid solution X were heated at temperatures below the decomposition temperature of the pure compound.

Åkermanite.—Many attempts have been made to explain the composition of the members of the melitite group of minerals (tetragonal in symmetry), and most of the resultant explanations have presupposed the existence of a mineral åkermanite. Vogt[44] assumed the formula of this pure compound to be 4CaO.3SiO$_2$ although usually part of the lime was "replaced" by magnesia or a like base. Day and Shepherd[45] were, however, unable to obtain any evidence of the existence of such a compound in their investigation of the lime-silica series of minerals. Later Rankin and Wright[46] noting the similarity between some of the properties ascribed to åkermanite and those of the compound 3CaO.2SiO$_2$ (orthorhombic in symmetry) suggested that the latter might be the åkermanite analogue in the binary system. More recently Schaller,[47] recognizing the ternary nature of the melitite group, has stated that the correct formula for this second compound is 8CaO.4MgO.9SiO$_2$.

Since the compound 4CaO.3SiO$_2$ has never been prepared in the pure state and there is little real evidence of its existence, this formula may be regarded as purely speculative.

The formula 8CaO.4MgO.9SiO$_2$ is based on Schaller's interpretation of two analyses[48] of a tetragonal Vesuvian mineral. This interpretation would need but little modification if the formula were written 2CaO.MgO.2SiO$_2$, corresponding to the tetragonal ternary compound of this system.

The essential optical properties of the analyzed åkermanite (1) and of the ternary compound (2) are compared as follows:

[44] T. H. L. Vogt, Mineralbildung in Schmelzmassen, 96, 1892.
[45] A. L. Day and E. S. Shepherd, this Journal, 22, 280, 1906.
[46] G. A. Rankin and F. E. Wright, this Journal 39, 1, 1915.
[47] W. T. Schaller, U. S. Geol. Survey, Bull. 610, 1916.
[48] See F. Zambonini, Mineralogià Vesuviana, 255, 1910.

$$\overset{\omega}{} \qquad \overset{\epsilon}{}$$

(1) 1·6332   1·639
(2) 1·631   1·638

We have been unable to prepare a compound or solid solution having more nearly the formula $8CaO.4MgO.$ $9SiO_2$. The compound $2CaO.MgO.2SiO_2$, as far as we know, forms no appreciable solid solutions.

In this connection attention may be called to the confusion which may arise from the use of such formulas as $4R''O.3SiO_2$ applied to minerals. For the sake of simplicity let us assume that we have a case in which $R''O$

FIG. 15.
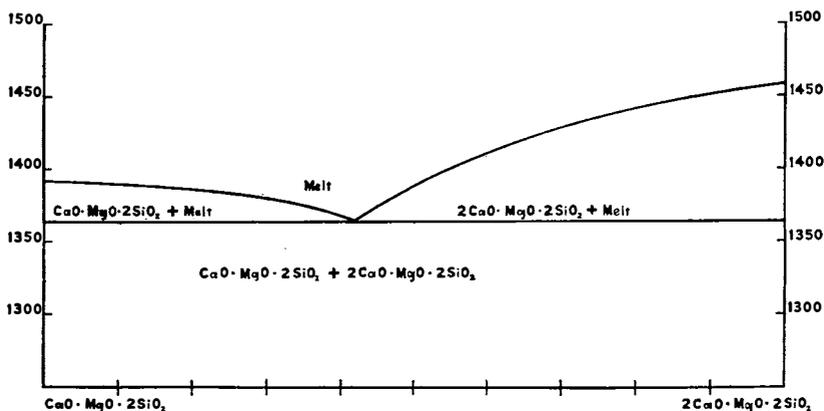
FIG. 15.—The binary system $CaO.MgO.2SiO_2$-$2CaOMgO.2SiO_2$. wt. per cent.

represents but two oxides.[49] As so used R'' may represent any one of three things: either (1) two elements in a definite ternary compound; or (2) two elements in solid solutions containing no ternary compounds, but only component oxides and binary compounds, or binary compounds alone; or (3) two elements in solid solution involving ternary compounds, either alone, or with binary compounds, or with component oxides or with both.

The tridymite-cristobalite inversion.

The tridymite-cristobalite transformation is very sluggish even when it takes place through solution.   Fenner[50]

[49] Similar statements would apply to minerals containing more than three components, but with additional complications.
[50] This Journal (4), 36, 331, 1913.

in his investigation of it used a flux of sodium tungstate. We have studied it in melts of our ternary system. We selected a composition, CaO 24, MgO 7, SiO₂ 69, which lies within the silica field and melts completely at 1536°C. The tridymite and cristobalite present in the various quenches made could not be separated and analyzed, therefore the only evidence that they are little if any affected by solid solution rests upon determinations of refractive index. The values obtained agree within ± 0·003 with those of purest natural crystals and with Fenner's values for material formed in molten sodium tungstate. Our observations are given below.

FIG. 16.
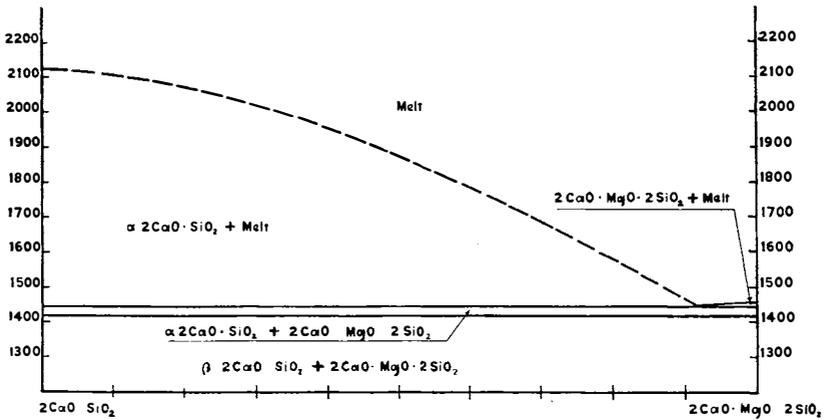
FIG. 16.—The binary system 2CaO.MgO2SiO₂-2CaO.SiO₂. wt. per cent.

1. A charge containing only tridymite plates and glass was prepared by heating the original material which contained cristobalite for 16 hours near 1370°C, the eutectic temperature being 1320°C. Portions of this charge were then given the following treatments.

    (a) Heated 5 hours at approximately 1530°C. The charge then contained much cristobalite.

    (b) Heated 5 hours at 1515°C and then 10 hours during which time the temperature fell to 1500°C. The charge contained cristobalite; no tridymite could be identified.

    (c) Heated 9½ hours at 1496°C. Much tridymite, no cristobalite identified.

Fig. 17.

α CaO · SiO₂ Solid Sol'n + Melt

Melt

α CaO · SiO₂ Solid Sol'n + Melt

α CaO · SiO₂ Solid Sol'n

2 CaO · MgO · 2SiO₂ + Melt

α CaO · SiO₂ Solid Sol'n + 2 CaO · MgO · 2 SiO₂

α C a O · SiO₂ Solid Sol'n + β CaO · SiO₂ Solid Sol'n

β CaO · SiO₂ Solid Sol'n

β CaO · SiO₂ Solid Sol'n + 2 CaO · MgO · 2 SiO₂

CaO · SiO₂
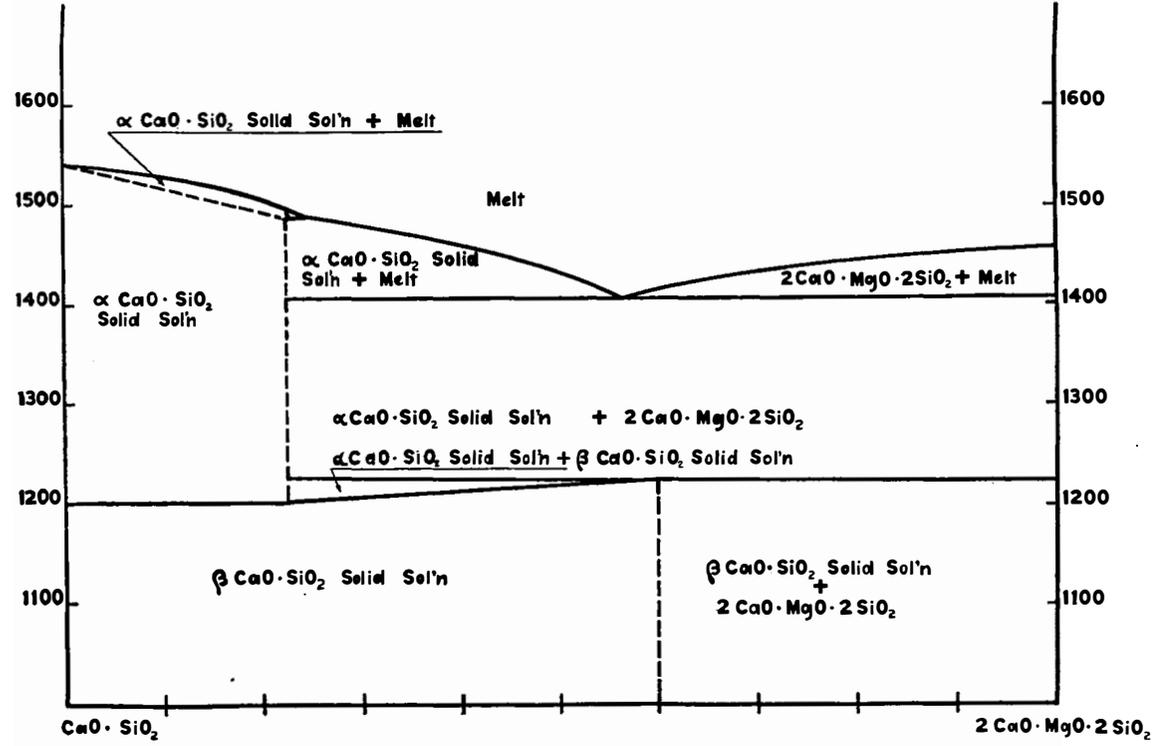
2 CaO · MgO · 2 SiO₂

FIG. 17.—The binary system CaO.SiO₂-2CaO.MgO.2SiO₂. wt. per cent.

2. The charge which contained only tridymite was mixed with some of the original material forming a charge containing both cristobalite and tridymite. This material was treated as follows:

   (*a*)   Heated at 1515° for 3 hours.   Both tridymite and cristobalite identified.
   (*b*)   Heated at 1485° for 3½ hours.   Both tridymite and cristobalite present.
   (*c*)   Heated for 16 hours, the temperature falling from 1500°C to 1483°C.   Little if any change.

3. A charge containing cristobalite + glass — heated all night at 1464°C.   No tridymite formed.

These results confirm the observations of both Fenner and Bowen[51] upon the sluggishness of this inversion, and because of this sluggishness it is impossible to fix upon an exact value for the inversion temperature in this system. Our results certainly indicate a value in this silicate system which lies below 1500°C with cristobalite as the stable high-temperature form. Fenner found in the tungstate melts, 1470 ± 10°C. Only slight, if any, solid solution could have been present to affect our measurements or Fenner's, which are in substantial agreement.

THE BINARY SYSTEMS WITHIN THE TERNARY SYSTEM.

The presence within the ternary system of so many compounds which melt incongruently and also so many solid solutions, renders the binary systems rather few in number. The systems $CaO.MgO.2SiO_2$—$2CaO.MgO.$ $2SiO_2$ and $2CaO.MgO.2SiO_2$—$2CaO.SiO_2$ are of the simplest type and are given diagrammatically in figures 15 and 16 which were obtained by interpolation from the melting temperatures determined for compositions lying in the fields of these compounds. The system $CaO.$ SiO_2—$2CaO.MgO.2SiO_2$ is more complicated including as it does several series of solid solutions. The evidence upon which the purely solidus relations are based will be given in a later paper but for the sake of completeness the general results are included in the diagram given in fig. 17.

[51] This Journal (4), **38**, 245, 1914.

In conclusion, thanks are due Dr. N. L. Bowen for his friendly criticisms and Mr. G. A. Rankin for certain preliminary results which he generously placed at our disposal at the commencement of the investigation.

SUMMARY.

The ternary system lime-magnesia-silica has proved to be the most complicated of the four possible ternary systems which may be constructed from the four oxides, lime, magnesia, alumina, and silica. The crystalline phases which are definite compounds and which appear as primary phases are as follows:

Lime; magnesia; silica (tridymite and cristobalite); $\alpha CaO.SiO_2$ (pseudowollastonite); $3CaO.2SiO_2$; α and β $2CaO.SiO_2$; $MgO.SiO_2$ (clino-enstatite): $2MgO.SiO_2$ (forsterite); $CaO.MgO.2SiO_2$ (diopside); $5CaO.2MgO.6SiO_2$ and $2CaO.MgO.2SiO_2$. The melting point of $2CaO.MgO.$ $2SiO_2$ is $1458° \pm 5°C$ and the decomposition temperature of $5CaO.2MgO.6SiO_2$ is $1365° \pm 5°C$.

In addition to these, crystals representing several solid solutions also appear as primary phases. The solid solutions are:

1. A complete series with clino-enstatite and diopside as end members, generally known as pyroxenes.

2. The pseudowollastonite solid solutions whose compositions form an area bounded by the following lines: (1) the $CaO.SiO_2$-$CaO.MgO.2SiO_2$ line; (2) a line running from the composition CaO, 44·4, MgO 3·1, SiO_2 52·5 on the above-mentioned line across to the composition CaO 46·7, MgO 3·5, SiO_2 49·8 on the $CaO.SiO_2$-$2CaO.MgO.$ $2SiO_2$ line; (3) then either the last-mentioned line back to $CaO.SiO_2$, or, more probably, an approximate continuation of line (2) to about the composition CaO 50, SiO_2 50, on the side line.

3. The wollastonite solid solutions; these extend to about 17 percent diopside or 3·2 percent MgO at the higher temperatures. The most concentrated of these solid solutions along the diopside line (the 17 per cent) decomposes at $1340° \pm 5°C$, and this solid solution is the only one represented on the liquidus.

4. The $5CaO.2MgO.6SiO_2$ solid solutions. Only a few of these solid solutions which are decomposed at the higher temperatures near the decomposition-temperature

of the pure compound are stable in contact with a suitable liquid.

5. Certain members of the monticellite solid solutions. Monticellite takes up forsterite in solid solution to the extent of about ten per cent and the decomposition temperature of the solutions is thereby raised. Monticellite itself probably decomposes at too low a temperature to ever occur at a primary phase.

The temperature-concentration relations of the liquids which may be in equilibrium with each of these phases have been thoroughly investigated where necessary by means of the quenching method, and the results obtained have been correlated with the existing data on the remainder of the ternary system.

The compounds $5CaO.2MgO.6SiO_2$ and $2CaO.MgO.2SiO_2$ have not been prepared previously. Attempts to prepare a compound of the formula $8CaO.4MgO.9SiO_2$ (Schaller's åkermanite) gave negative results.

The monticellite solid solutions and the compound åkermanite are discussed at length but the wollastonite and the $5CaO.2MgO.6SiO_2$ solid solutions are only briefly mentioned as they will be made the subject of a subsequent paper.

Experiments were made on the tridymite-cristobalite inversion temperature, which was found, for this system, to be below $1500°C$, in approximate agreement with Fenner's original value of $1470°$; the great sluggishness of the inversion precluded a more exact determination on our part.

Geophysical Laboratory, Carnegie Institution of Washington, Washington, D. C., April, 1919.