ART. XIX.—*The Ternary System: Diopside—Forsterite—Silica*; by N. L. BOWEN.

CONTENTS:

INTRODUCTION.

THE system dealt with in the present paper is a part of the more general ternary system CaO–MgO–SiO_2, and is that part which is probably of greatest interest to the petrologist, since, among the solid phases, there are representatives of the important rock-forming mineral groups, the pyroxenes and the olivines.

The compound diopside, $CaMgSi_2O_6$, was studied formerly at this laboratory* in an investigation of the system $CaSiO_3$–$MgSiO_3$. This system was treated as binary, but recent work† has shown that the compound $MgSiO_3$ is unstable at its melting point and can itself be treated only as part of a two-component system. It is necessary, therefore, to treat the system $CaSiO_3$–$MgSiO_3$, or at least the portion of it $CaMgSi_2O_6$–$MgSiO_3$, as a part of the ternary system $CaMgSi_2O_6$–Mg_2SiO_4–SiO_2. The present paper, which deals with this ternary system, is, therefore, essentially a revision of former work on $CaMgSi_2O_6$ and $MgSiO_3$, in which it has been found necessary to study completely the field of the ternary system.

Method of Working.

The mixtures used were made up from specially purified silica, calcium carbonate, and magnesia obtained by igniting the carbonate to constant weight. Equilibrium was studied by the method of quenching, which consists in holding a small charge of known composition at a measured temperature for a period of time and then chilling instantly to room temperature. The charge is then examined under the microscope and the phases present are determined.

The phases found represent equilibrium at the furnace temperature for inert bodies like the silicates, unless there exists a readily reversible inversion in a solid phase, in which case the low temperature form may be found under the microscope whereas the high temperature form existed in the furnace. In such cases the solid phase nearly always gives evidence of having passed through this inversion.

The furnace used was a platinum resistance furnace and the temperature was measured by means of a Pt:Pt–Rh thermoelement which was calibrated by quenching charges of pure artificial minerals of known melting-point.

One point, however, namely the melting-point of the compound forsterite, was determined by observing directly the phenomenon of melting in an iridium furnace, the temperature being measured optically. This method of determining the temperature at which a mixture becomes visibly fluent is satisfactory for fixing the melting temperature of a compound or a eutectic when these form thin liquids, but cannot be relied

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* Allen, White, Wright and Larsen: Diopside and Its Relation to Calcium and Magnesium Metasilicates, this Journal (4), xxvii, 1, 1909.

† Bowen and Andersen, this Journal (4), xxxvii, 487, 1914.

upon in determining points on the liquidus intermediate between a eutectic and a compound. Some investigators* have, however, used this method on these intermediate compositions, although a little consideration would make it clear that such compositions will soften either at the eutectic point or at some temperature intermediate between the eutectic and the liquidus point, but always well below the liquidus.

THE BINARY SYSTEMS.

The results obtained in the three binary systems will first be presented.

The System Mg_2SiO_4–SiO_2.

The system Mg_2SiO_4–SiO_2 has been described in a former publication which deals with the system MgO–SiO_2.† The equilibrium diagram is given in fig. 1. The principal feature of this system is the fact that the compound $MgSiO_3$ (clinoenstatite) is unstable at its melting-point, breaking up at 1557° into liquid and forsterite. The details of the system are given in the paper referred to.

The System $CaMgSi_2O_6$–SiO_2.

The system, diopside-silica, shows the simple eutectic relation (fig. 2). Diopside melts at 1391°. The eutectic between diopside and tridymite is at 1362° and at the composition, diopside 84 per cent, silica 16 per cent.

The quenching experiments by which the figure was determined are tabulated below (Table I).

The liquidus for silica was determined up to 1580°, approximately the limit of safety with the platinum resistance furnace. Though the quenching experiments do not definitely prove its existence, a break on the silica liquidus is shown at 1470°, corresponding to the inversion point tridymite-cristobalite found by Fenner.

Lime-Magnesian Amphibole.—In one of the mixtures containing diopside 85 per cent and silica 15 per cent, which was melted and quickly cooled, crystals were found which, in general appearance, were very similar to the amphibole obtained when $MgSiO_3$ is quickly cooled. The crystals have, however, considerably higher refractive indices than the magnesian amphibole and probably are a lime-magnesian amphibole. The exact composition cannot be decided upon, inasmuch as the material was obtained only in the viscous mixture containing excess silica. It is probable that the viscosity of the mixture and the quick cooling condition the formation of this amphi-

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* Deleano, V. S., Zs. anorg. Chemie, lxxxiv, 401, 1914.

† Bowen and Andersen, this Journal (4), xxxvii, 487.

bole, as has been found to be true of the pure magnesian amphibole.*

The refractive indices are $\gamma = 1{\cdot}638 \pm {\cdot}003$, $\alpha = 1{\cdot}620 \pm {\cdot}003$. Optical character +, 2V about 45°. Occasional markings suggesting the amphibole cleavage of 120° were observed.

Fig. 1.

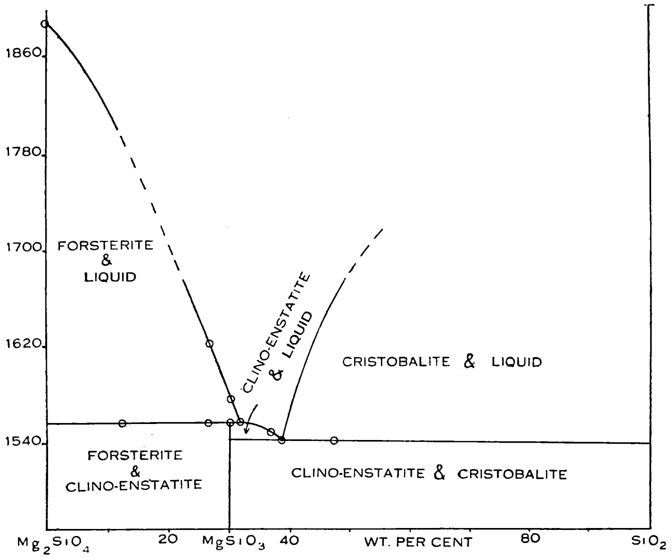

Table I.

Composition		Initial condition	Temperature	Time	Result
Diopside	SiO_3				
90	10	crystalline	1360	1 hr.	all crystalline
“	“	“	1365	1 hr.	glass and diopside
“	“	“	1375	1 hr.	glass and diopside
“	“	“	1380	1 hr.	glass only
85	15	“	1360	1 hr.	all crystalline
“	“	“	1364	1 hr.	glass and diopside
83	17	“	1364	1 hr.	glass and tridymite
80	20	“	1448	2 hrs.	glass and cristobalite
“	“	“	1453	¼ hr.	glass only
75	25	“	1577	2 hrs.	glass and cristobalite
“	“	“	1583	½ hr.	glass only

The System $CaMgSi_2O_6$–Mg_2SiO_4.

The system diopside-forsterite also shows the eutectic relation (fig. 3). The eutectic point, at the composition forsterite 12 per cent, diopside 88 per cent, is only about 4°–5° lower than

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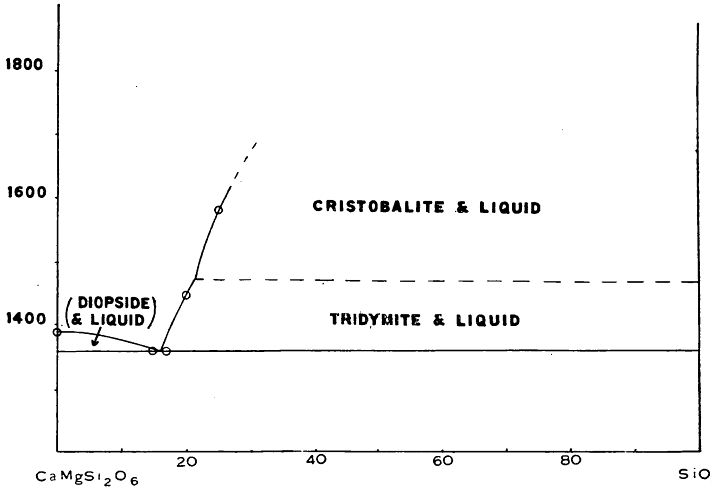
* Allen, Wright and Clement: Minerals of the Composition $MgSiO_3$, this Journal (4), xxii, 434, 1906.

the melting-point of diopside. There is no appreciable solid solution. When the mixture diopside 95 per cent, forsterite 5 per cent is crystallized both forsterite and diopside appear in the product. The very slight lowering of the melting-point is, therefore, not due to solid solution of forsterite in the diopside. An explanation is offered towards the end of this paper under the heading, "Freezing-point Lowering in Silicate Melts."

FIG. 2.



The liquidus for forsterite was not determined above 1552° and the upper part is, therefore, shown as a dotted curve extending to the melting-point of forsterite. The quenching experiments on the system are tabulated below.

TABLE II.

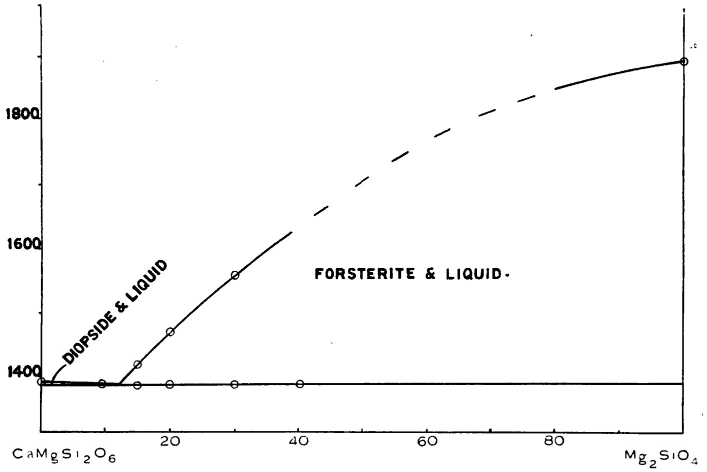
Composition		Initial condition	Temperature	Time	Result
Diopside	Forsterite				
90	10	crystalline	1386°	½ hr.	no change
"	"	"	1389°	½ hr.	glass and diopside
85	15	"	1389°	½ hr.	glass, forsterite and diopside
"	"	"	1391°	½ hr.	glass and forsterite
"	"	"	1412°	½ hr.	glass and forsterite
"	"	"	1415°	½ hr.	glass only
80	20	"	1448°	½ hr.	glass and forsterite
"	"	"	1453°	½ hr.	glass only
70	30	"	1550°	½ hr.	glass and forsterite
"	"	"	1554°	½ hr.	glass only
60	40	"	1600°	½ hr.	glass and forsterite

The Ternary System.

Preliminary Statement.

The problem in the ternary system is the location of the fusion surface for each of the solid phases. Considering composition alone, the solution of the problem consists in the delimiting of the *fields* for the various solid phases. The *field* for solid phase A is such that it includes all the points representing the composition of all the liquids which can exist in equilibrium with solid A. Considering temperature alone, the solution of the problem consists in finding the temperature at which crystallization begins (or melting is complete) in each mixture.

Fig. 3.



The method of quenching is particularly useful in the solution of the problem. If a mixture of known composition is held at various temperatures and the temperature is determined at which the last crystals, say A, disappear (dissolve in the liquid), then it is known that the composition dealt with lies in the field of A and the temperature of the fusion surface for that composition is also determined. (The crystals which disappear last on heating are also those which appear first on cooling and are called the *primary phase.*) If a mixture of a different composition is taken and the primary phase is found to be B, then it is known that the *boundary curve* between the fields of A and B lies between these two compositions. By taking intermediate mixtures, a point on the boundary curve is fixed between as narrow limits as possible. Another series of mixtures fixes another point on the boundary curve and so the whole curve may be located. The same work fixes the temperature of a number of points on the boundary curve. It is apparent from the foregoing that all liquids lying on the boundary curve between the fields of A and B are in equilibrium with A and B.

The results are best expressed graphically by means of a solid figure in which composition is plotted horizontally, on triangular coördinates, and temperature vertically. For representation on a plane surface, composition is plotted on triangular coördinates and temperature is indicated by means of *isotherms*.

In the three binary systems there are a total of five solid phases,—diopside, cristobalite, tridymite, clino-enstatite and forsterite. The expectation is, therefore, that in the ternary diagram each would have its field, i. e. that there would probably be five fields, six boundary curves, and three ternary invariant points.* The equilibrium diagram would then have the general form shown in fig. 4.

An equilibrium diagram analogous to fig. 4 would be the result if there were no solid solution or only limited solid solution between any of the solid phases. In the actual case, however, the equilibrium diagram is very different, for clino-enstatite and diopside form an unbroken series of solid solutions, monoclinic pyroxenes. The result is that clino-enstatite, diopside and all the intermediate pyroxenes have but one field in common, and there are, therefore, only three boundary curves and only one ternary invariant point; viz. that corresponding with the equilibrium,—cristobalite, tridymite, pyroxene, and liquid (fig. 5).

It is now necessary to tabulate the quenching experiments which gave the results outlined above. The composition of any point in the triangle can, of course, be expressed in terms of the three components at its corners, but the composition is more readily visualized if the triangle is considered divided into two parts by the *pyroxene conjugation-line* and the composition of a point in the one part expressed as pyroxene of a certain composition + silica and, in the other part, as pyroxene + forsterite. In the tables this latter method will be followed. The abbreviation En will be used to indicate the composition $MgSiO_3$ and Di to indicate $CaMgSi_2O_6$. The abbreviations are not intended to imply anything concerning the state of crystallization of the mixture. Thus an uncrystallized mixture (glass) of composition $CaMgSi_2O_6$ 60 per cent, $MgSiO_3$ 40 per cent would be indicated Di 60 En 40.

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* Such points are, of course, invariant only when the system is considered as a condensed system.

TABLE III.

Boundary Curve, Forsterite-Pyroxene.

Composition		Initial condition	Temperature	Time	Result
Pyroxene	SiO_2				
90 (En 81 Di 19)	10	crystalline	1510°	1 hr.	glass only
"	10	"	1516	1 hr.	glass and pyroxene
95 (En 81 Di 19)	5	"	1520	1 hr.	glass and pyroxene
"	"	"	1524	1 hr.	glass only
97 (En 81 Di 19)	3	"	1525	1 hr.	glass, pyroxene and forsterite
"	"	"	1529	1 hr.	glass only
95 (En 63 Di 37)	5	"	1486	1 hr.	glass only
"	"	"	1482	1 hr.	glass and pyroxene
97 (En 63 Di 37)	3	"	1485	1 hr.	glass, pyroxene and forsterite
"	"	"	1490	1 hr.	glass only
97 (En 44 Di 56)	3	"	1430	1 hr.	glass and pyroxene
"	"	"	1435	1 hr.	glass only
98 (En 44 Di 56)	2	"	1432	1 hr.	glass, pyroxene and forsterite
100 (En 25 Di 75)	0	"	1410	1 hr.	glass and forsterite
98 (En 25 Di 75)	2	"	1407	1 hr.	glass and pyroxene
"	"	"	1410	1 hr.	glass only
100 (En 20 Di 80)	0	"	1390	1 hr.	glass and pyroxene
"	"	"	1392	1 hr.	glass only
Pyroxene	Mg_2SiO_4				
98 (En 17 Di 83)	2	"	1390	1 hr.	glass and pyroxene
96 (En 17 Di 83)	4	"	1392	1 hr.	glass and forsterite

Boundary Curve, Pyroxene-Silica.

Pyroxene	SiO_2				
85 (En 81 Di 19)	15	crystalline	1516°	2 hrs.	glass and cristobalite
"	13	"	1516	2 hrs.	glass and pyroxene
85 (En 63 Di 37)	15	"	1483	2 hrs.	glass, pyroxene and cristobalite
"	"	"	1487	2 hrs.	all glass
85 (En 44 Di 56)	15	"	1436	2 hrs.	glass, tridymite and cristobalite
"	"	"	1429	2 hrs.	glass, tridymite and pyroxene
87 (En 44 Di 56)	13	"	1431	2 hrs.	glass and pyroxene
85 (En 25 Di 75)	15	"	1400	2 hrs.	glass and tridymite
"	"	"	1390	2 hrs.	glass and tridymite
"	"	"	1380	2 hrs.	glass, tridymite and pyroxene
87 (En 25 Di 75)	13	"	1380	2 hrs.	glass, tridymite and pyroxene
"	"	"	1384	2 hrs.	glass only
85 (En 17 Di 83)	15	"	1370	2 hrs.	glass and rare tridymite
"	"	"	1368	2 hrs.	glass, tridymite and pyroxene
85 (En 7 Di 93)	15	"	1368	2 hrs.	glass and tridymite
"	"	"	1366	2 hrs.	glass, tridymite and pyroxene

TABLE III (continued).

Points on Silica Surface.

Composition			Initial condition	Temperature	Time	Result
	Pyroxene	SiO_2				
80	En 81 Di 19)	20	crystalline	1610°	1 hr.	glass and cristobalite
	"	"	"	1620	1 hr.	glass only
80	(En 63 Di 37)	20	"	1587	1 hr.	glass and cristobalite
	"	"	"	1593	1 hr.	glass only
80	(En 44 Di 56)	20	"	1556	1 hr.	glass and cristobalite
	"	"	"	1562	1 hr.	glass only
80	(En 25 Di 75)	20	"	1538	1 hr.	glass and cristobalite
	"	"	"	1543	1 hr.	glass only
80	(En 17 Di 83)	20	"	1502	1 hr.	glass and cristobalite
	"	"	"	1507	1 hr.	glass only
	Points on Pyroxene Surface.					
92	(En 72 Di 28)	8	crystalline	1504°	1 hr.	glass and pyroxene
	"	"	"	1508	1 hr.	glass only
92	(En 53 Di 47)	8	"	1461	1 hr.	glass only
	"	"	"	1457	1 hr.	glass and pyroxene
92	(En 44 Di 56)	8	"	1427	1 hr.	glass and pyroxene
	"	"	"	1432	1 hr.	glass only
92	(En 35 Di 65)	8	"	1407	1 hr.	glass and pyroxene
	"	"	"	1413	1 hr.	glass only
92	(En 25 Di 75)	8	"	1390	1 hr.	glass only
	"	"	"	1386	1 hr.	glass and pyroxene
92	(En 7 Di 93)	8	"	1377	1 hr.	glass and pyroxene
	"	"	"	1382	1 hr.	glass only
	Points on Fosterite Surface.					
100	(En 81 Di 19)		crystalline	1550°	½ hr.	glass and forsterite
			"	1554	½ hr.	glass only
100	(En 72 Di 28)		"	1534	½ hr.	glass only
			"	1530	½ hr.	glass and forsterite
100	(En 63 Di 37)		"	1512	½ hr.	glass and forsterite
			"	1516	½ hr.	glass only
100	(En 53 Di 47)		"	1490	½ hr.	glass and forsterite
			"	1494	½ hr,	glass only
100	(En 44 Di 56)		"	1459	½ hr.	glass and forsterite
			"	1464	½ hr.	glass only
100	(En 35 Di 65)		"	1428	½ hr.	glass and forsterite
			"	1432	½ hr.	glass only
100	(En 25 Di 75)		"	1393	½ hr.	glass and forsterite
			"	1397	½ hr.	glass only
	Pyroxene	Forsterite				
80	(En 33 Di 67)	20	"	1550	½ hr.	glass and forsterite
	"	"	"	1555	½ hr.	glass only
90	(En 25 Di 75)	10	"	1468	½ hr.	glass and forsterite
	"	"	"	1472	½ hr.	glass only
80	(En 17 Di 83)	20	"	1518	½ hr.	glass and forsterite
	"	"	"	1523	½ hr.	glass only
89	(En 13 Di 87)	11	"	1430	½ hr.	glass and forsterite
	"	"	"	1434	½ hr.	glass only
92	(En 13 Di 87)	8	"	1407	½ hr.	glass and forsterite
	"	"	"	1412	½ hr.	glass only

Fig. 4.

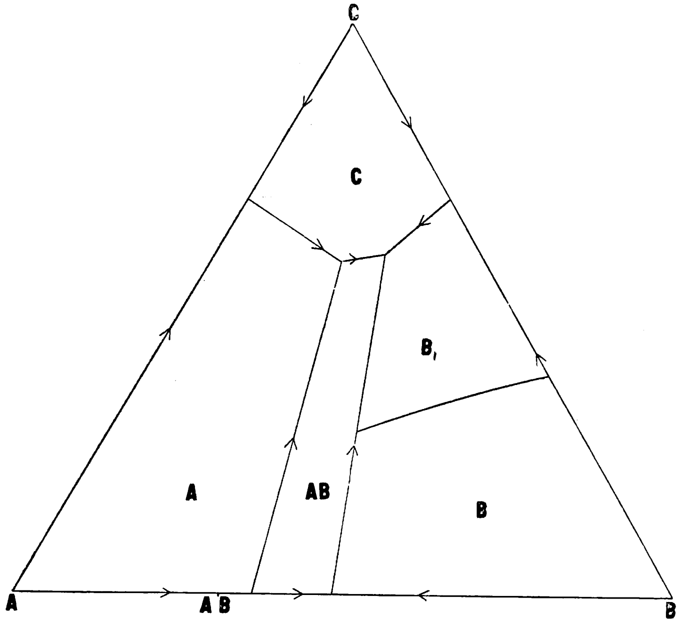

C
C
B₁
A
AB
B
A
A B
B

Fig. 5.

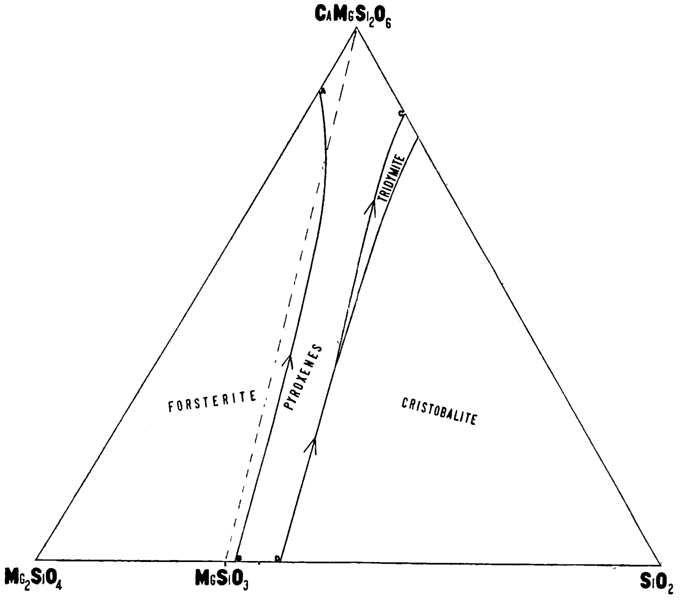
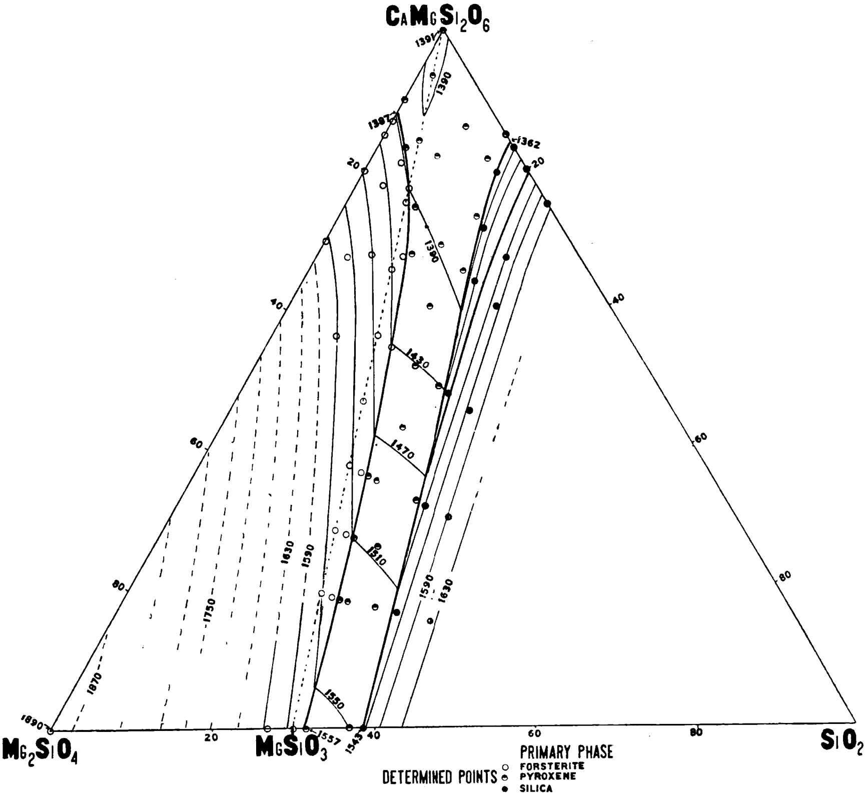

CaMgSi₂O₆
A
C
TRIDYMITE
PYROXENES
FORSTERITE
CRISTOBALITE
B
D
Mg₂SiO₄
MgSiO₃
SiO₂

Fig. 6.



General Character of the Fusion Surfaces.

In fig. 5 the boundary curves are drawn in accordance with the results stated in Table III. In fig. 6 the determined points are indicated and the isostherms drawn as far as they are fixed by these points. All points on the pyroxene surface are determinable by the quenching method. In the forsterite field and in the silica field only points below 1625° (usually below 1580°) were determined. The pyroxene surface is one of relatively gentle gradient, falling from the more magnesian mixtures towards the more calcic. The forsterite surface mounts steeply towards forsterite (melting-point 1890°). The silica surface mounts still more steeply, in its determinable part, towards silica.

The Melting Point of Cristobalite.

In the paper on the system MgO–SiO_2[*] it was stated that indications were found that the liquidus of cristobalite is very steep close to the eutectic, clino-enstatite-cristobalite. The statement was made in this tentative form because it was considered possible that equilibrium had not been obtained in these rather siliceous mixtures. Later work has, however, shown that equilibrium between liquid and solid is readily attained in these mixtures and that points on the cristobalite liquidus can be fixed with precision. The points found in the diopside-silica system, in the clino-enstatite-silica system and several intermediate points in the ternary system all agree in showing that the silica surface is very steep.

It is true that a lessening of the gradient is shown at the higher attainable temperatures (note spacing of the isotherms as fixed by determined points fig. 6) so that the silica surface may not mount as high as the steep gradient at lower temperatures would suggest. Nevertheless it is clear that the indicated melting point of cristobalite must be higher than 1625°, the value found by Fenner,[†] higher than 1685° even, the value found by Endell and Rieke.[‡]

The mixture $MgSiO_3$ 75 per cent, SiO_2 25 per cent held at 1625° for one hour gives glass and considerable cristobalite, an amount which would require a raising of the temperature 40°–50° to effect its solution. This estimate (40°–50°) may be made with considerable assurance on the basis of much experience with quenchings of mixtures in the silica field. Even at the composition 25 per cent SiO_2, then, the liquidus is well above 1625°. I do not know how to reconcile these determinations with the evidences of melting found in cristobalite by Fenner at 1625° and by Endell and Rieke at 1685° unless it is as Dr. Fenner has suggested to me, that cristobalite has a variable molecular constitution and a similarly variable melting-point according to the conditions under which it is formed, a peculiarity which he has shown to be true of its low-temperature inversion. In the various mixtures used in the present work, in which the cristobalite is crystallized simply by cooling the molten mixture, there is no evidence of variability. All the points on the silica surface are entirely consistent with each other, a fact which probably indicates that true equilibrium is obtained between the various molecules which make up the solid phase, cristobalite.

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[*] Bowen and Andersen, this Journal (4), xxxvii, 487, 1914.

[†] Fenner, C. N., The Stability Relations of the Silica Minerals, this Journal, (4), xxxvi, 381, 1913.

[‡] K. Endell and R. Rieke, Zs. anorg. Chem., lxxix, 239-259, 1912.

The fact that equilibrium is readily obtained between solid and liquid in these melts, and that the high temperature of the points found is not due merely to a sluggishness in the solution of cristobalite, was shown in a manner which is illustrated by the following example. The completely crystallized mixture diopside 75 per cent, SiO_2 25 per cent was held at 1575° for periods varying from 15 minutes up to 5 hrs. In each case the resultant product was glass and a very little cristobalite. On the other hand the same mixture, again completely crystalline, was held at 1585° for only 15 minutes and the product is pure glass without cristobalite. This same method of checking the temperatures of the silica surface was applied to all the points except those above 1600°. It is not advisable to hold the furnace at these higher temperatures for a period of 5 hrs., but since it has been shown above that a period of 15 minutes is sufficient to obtain equilibrium, holding the mixture for one hour, as was done for example with the mixture $MgSiO_3$ 75 per cent, SiO_2 25 per cent at 1625°, provides an ample margin of safety to insure equilibrium.

Fig. 7.

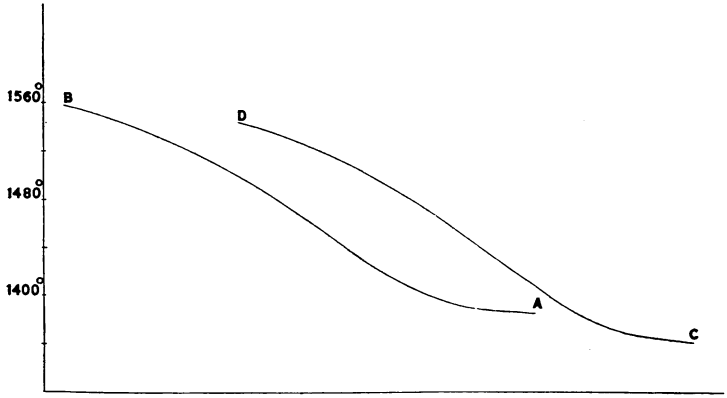


Fig. 7. Vertical sections along boundary curves. AB forsterite-pyroxene, CD pyroxene-silica.

It may therefore be repeated that the results point consistently to a melting-point of cristobalite much higher than 1625°. Cristobalite formed by other methods and consisting of various molecules in *metastable* equilibrium in the single solid phase may, however, show a beginning of melting at the lower temperatures found by Fenner and by Endell and Rieke.

General Character of the Boundary Curves.

The composition diagram, with isotherms, is a scheme for representing both composition and temperature on a plane surface (in plan). It is a projection, on the plane of the base, of the solid figure showing the fusion surfaces. Now a vertical section of the solid figure shows the temperature relations somewhat more clearly than do the isotherms, just as a vertical section along a given direction in a mapped area shows the relief more strikingly than does a contoured map. Fig. 7 has therefore been drawn to show the temperatures along the boundary curves. It represents vertical sections of the solid figure along the boundary curves. Composition is, of course, not indicated and is known only by referring the curves to their position on the composition diagram.

The figure shows that the boundary curve, forsterite-pyroxene, falls continuously, becomes gradually flatter as it approaches the point where it cuts the pyroxene conjugation line and thenceforth is nearly flat.

The boundary curve pyroxene-silica is, strictly speaking, composed of two boundary curves, pyroxene-cristobalite and pyroxene-tridymite. The difficulty of getting silica to assume the equilibrium form in the neighborhood of the inversion point tridymite-cristobalite (1470°) is very great and in quenchings near this temperature both forms were usually found. Any sudden change of direction which this boundary curve may have at the inversion temperature is, therefore, not discoverable experimentally. The two curves may, for convenience, be considered as the one boundary curve pyroxene-silica.

The pyroxene-silica boundary falls continuously from the eutectic, clino-enstatite-silica to the eutectic diopside-silica. It becomes considerably flattened at the lower temperatures, but there is clearly a continuous fall, without a minimum.

Such boundary curves can be interpreted only in terms of complete solid solution between diopside and clino-enstatite, a fact which is confirmed by other evidence presented later.

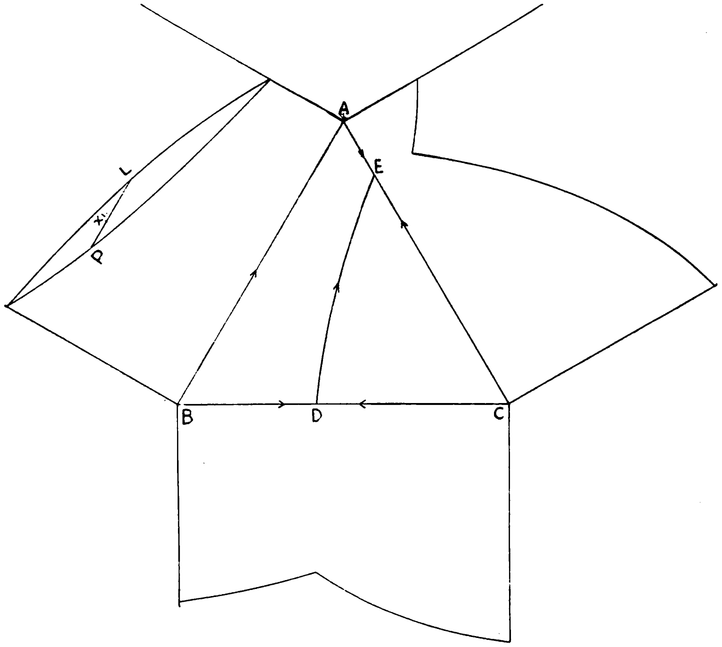
Brief Theoretical Discussion of Solid Solution in Ternary Systems.

The relations in the present system are somewhat complex and, so far as the writer is aware, a system showing the same general relations has not been investigated nor has such a system received theoretical treatment. Before proceeding further with the discussion of the equilibrium diagram it would, therefore, be well to discuss some theoretical cases of solid solution in ternary systems which have been treated by

Schreinemakers.* No attempt is made to discuss all possible cases. Attention is confined to systems which lead up to that under investigation.

One simple case is shown in fig. 8. Here the two components A and B form a complete series of solid solutions and each forms a eutectic with C. These relations, in the binary systems, are shown in the diagrams erected on the sides of the triangle. As will be noted, the arrows indicate, in the ternary diagram, the direction of *falling* temperature, a method maintained throughout the present paper.

FIG. 8.



All liquids of composition represented by a point in the area ABDE may exist in equilibrium with a solid solution A + B. All liquids in the area DEC may exist in equilibrium with C and all liquids lying along the curve DE may exist in equilibrium with both solid C, and a solid solution A + B.

Fig. 9 shows the relations at any temperature T°. LNM is the isotherm for temperature T°. The phases present for various compositions at this temperature are as follows:

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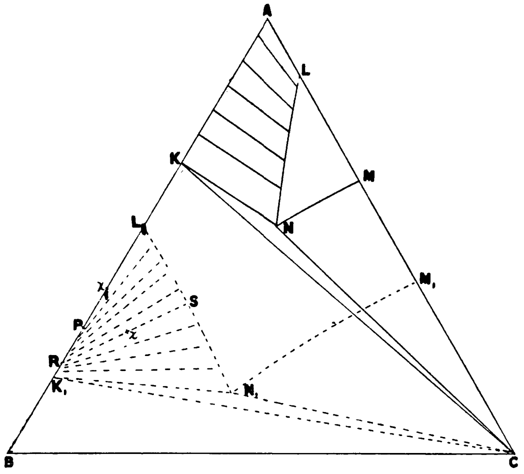
* Zs. phys. Chem., l, 169; li, 547.

area LNM	all liquid
ALKN	liquid L to N and solid solution A to K.
MNC	liquid M to N and solid C.
KNC	liquid N, solid solution K, and solid C.
KCB	solid C and solid solution K to B.

Fig. 9.



At a higher temperature T_1° for which $L_1N_1M_1$ is the isotherm the relations are indicated by the dotted lines:

area $AL_1N_1M_1$	all liquid
$L_1N_1K_1$	liquid N_1 to L_1 and solid solution P–K_1
M_1N_1C	liquid M_1 to N_1 and solid C
K_1N_1C	liquid N_1, solid solution K_1 and solid C
K_1CB	solid C and solid solution K_1 to B.

The lines crossing the fields ALNK for the temperature T°, and $L_1K_1N_1$ for the temperature T_1° join the composition of a liquid with that of the solid solution which is in equilibrium with it. Thus at T_1° a mixture of total composition x consists of solid solution R and liquid S, and a mixture of total composition x_1 consists of liquid L_1 and solid solution P, a relation which is shown in the binary system in fig. 8.

The lines KN, K_1N_1, RS, etc., might be referred to as *solid-phase-indicating lines* since they indicate the composition of the solid-phase which is in equilibrium with various liquids. KN and K_1N_1 are special cases of solid-phase-indicating lines since they are also the boundaries of the three-phase field. It will be necessary to refer to lines of this type in general terms later and the name *three-phase-boundaries* will be used.

Since the points N and N_1 represent the composition of liquids in equilibrium with two solid phases they evidently would lie on the boundary curve DE of fig. 8. From each

FIG. 10.

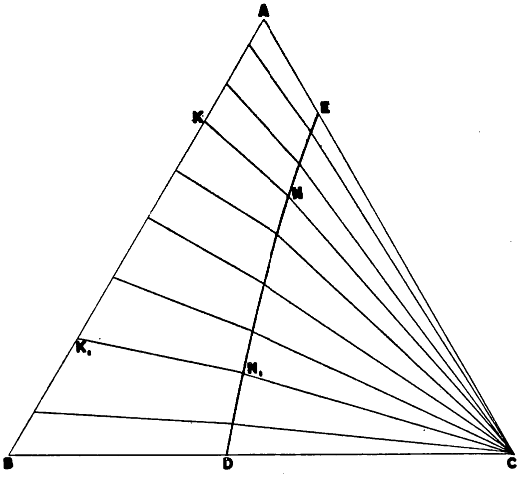
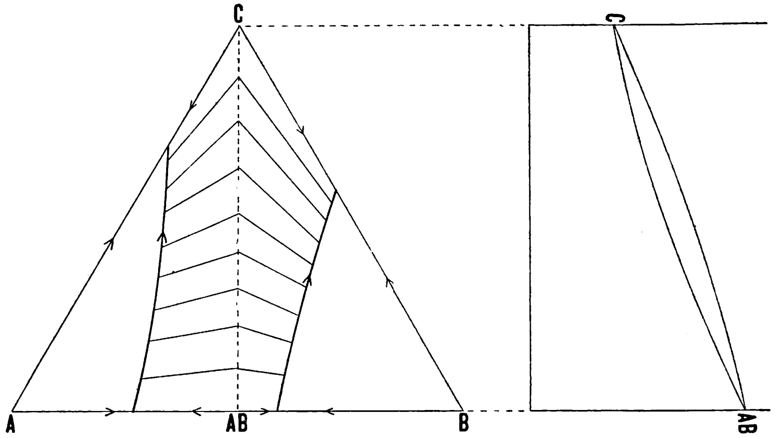


FIG. 11.



point along the boundary curve lines corresponding with NK and N_1K_1 and with NC and N_1C may be drawn. A set of these lines is shown in fig. 10. They are the three-phase-boundaries for various temperatures and indicate the composition of the solid phases which can exist in equilibrium with liquids represented by the various points along DE.

The three-phase-boundaries NC, N_1C, etc., are simply lines radiating from the composition of the pure solid C and require no special discussion. The three-phase-boundaries NK, N_1K_1, etc., crossing the solid solution field, have a specific direction determined by the properties of the system. Their usefulness in discussing the crystallization of a mixture will appear later.

Figure 11 illustrates the case of a ternary system in which the components A and B form a stable compound AB and this compound gives a complete series of solid solutions with the third component C. In this case two systems of the type of fig. 8 are combined; each half C–A–AB and C–B–AB may be treated separately and C–AB is a simple binary system of the type shown in the side figure. The three-phase-boundaries would then be of the type indicated in the figure (fig. 11).

After discussing these simpler systems the case of a compound unstable at its melting point, as in the system under investigation, may now be proceeded with. In fig. 12 is shown a theoretical case similar to the system under investigation. We cannot in this case divide the system into two ternary systems, and the system C–AB cannot be treated as a binary system. A solid solution of any composition between C and K behaves on melting as a true binary mixture and its behavior is expressed by the binary partial-diagram of the side figure (a). A solid solution of any composition between K and L behaves on melting as a true binary mixture until the temperature of the isotherm passing through the point K is reached and its behavior is again expressed by the side diagram up to this temperature, but with further rise of temperature the component A begins to separate and the mixture no longer behaves as a binary mixture. With solid solutions between L and AB liquid begins to form and the component A begins to separate simultaneously at a temperature higher than that of the point K, the behavior throughout the melting being that of a ternary mixture. The three-phase-boundaries of this system are of the type shown in fig. 12: NP, MP, N_1P_1, M_1P_1, etc.

There may, also, be a minimum on the solid-solution line between K and C as shown in fig. 12 (b). Accompanying this there may be (or may not be) a minimum on one or both of the boundary curves. The system investigated falls under the type of fig. 12 (b). There is a very flat ill-defined minimum close to diopside. On the boundary curves, as we have seen, there are no minima.

Fig. 12.

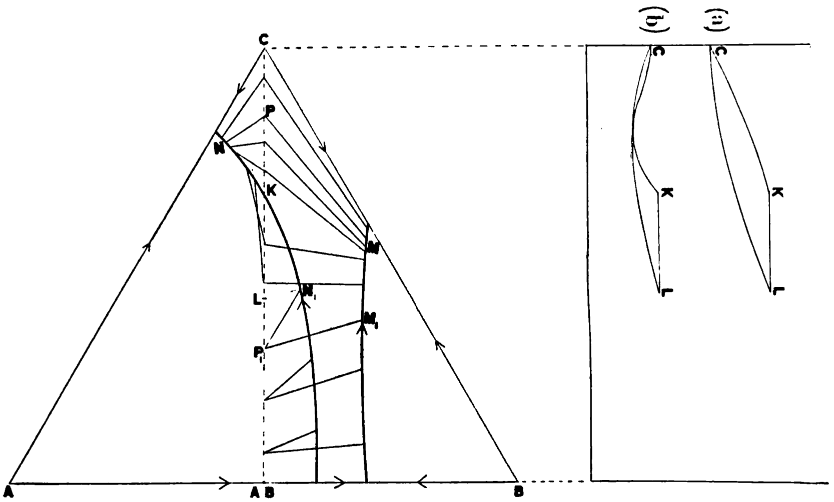
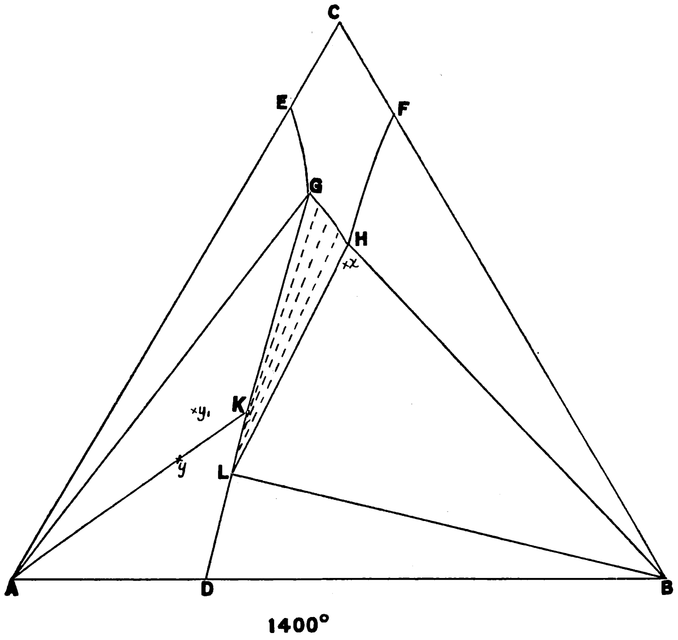


Fig. 13.



Methods of Determination of the Three-Phase-Boundaries.

The Composition Method.—After discussing theoretical systems of various types, we shall now return to the system under investigation and point out the methods used in determining the three-phase-boundaries.

Figure 12 indicates the relations at 1400°. The phases present for various compositions at equilibrium are as follows:

area	ECFHG	all liquid
	EGA	liquid E to G and forsterite
	GKA	liquid G, pyroxene K and forsterite
	KAD	forsterite and pyroxene K to D
	LDB	tridymite and pyroxene L to D
	LHB	liquid H, pyroxene L and tridymite
	HBF	liquid H to F and tridymite
	KLHG	liquid G to H and pyroxene K to L.

The lines GK and HL are evidently three-phase-boundaries.

In order to determine this figure experimentally it is necessary to know the position of the isotherm EGHF for 1400° especially of the points G and H which lie on the two boundary curves of fig. 6. The temperature of all points along the boundary curves has already been experimentally determined (fig. 6). It is now necessary only to determine the points K and L. The point L can be fixed by taking any mixture in the triangle CBD, that is, any mixture of pyroxene and silica and holding it at 1400°. If it is all liquid, or if it consists of liquid and only one solid phase, another composition must be tried until one is found which at 1400° consists of liquid and the solid phases pyroxene and tridymite. If the composition of the pyroxene can now be determined, the point L is thereby determined. The pyroxene cannot be separated and analyzed, but its composition can be determined fairly closely by optical methods and the point L approximately fixed. In the actual procedure it is never necessary to try a number of mixtures as it might appear to be from the above discussion. If a mixture corresponding to a point (x) on (or very close to) the boundary curve at a temperature slightly higher than 1400° is used, the desired result, viz., two solid phases and liquid, will necessarily be obtained.

In a similar manner the point K can be determined. A mixture which at 1400° will give forsterite and pyroxene is held at 1400° and the composition of the pyroxene (point K) determined optically. By working at other temperatures the three-phase-boundaries (lines corresponding with GK and HL) for various temperatures can be approximately fixed by this method of determining the composition of the pyroxene in a three-phase mixture (the composition method).

The Temperature Method.—The three-phase-boundaries can be determined by another method which gives more accurate results. Any composition along the line AK (fig. 13) shows the two solid phases pyroxene and forsterite at 1400°. If the temperature is raised a very little, liquid begins to form. This fact may be used to determine the figure corresponding to fig. 13 for any temperature. Thus if a mixture of composition y is held at various temperatures and the temperature of beginning of melting determined, this will be found to be 1400°. If a mixture of composition y_1 is taken it is found to begin to melt at a somewhat lower temperature. If, then, Ay_1 is produced to meet the pyroxene line CD at K_1 and the point G_1 on the isotherm for this lower temperature is joined with the point K_1, the line K_1G_1 will be the three-phase-boundary for this temperature.

It is easy to see that the three-phase-boundaries LH and L_1H_1 can be determined in a similar manner, namely, by finding the temperatures at which various mixtures of pyroxene and silica begin to melt. This method (the temperature method) is more accurate than the composition method and was the one followed. The results were confirmed by the composition method in some instances during the course of some experiments in which pyroxenes of various compositions were prepared, for optical purposes, by holding a mixture at a temperature at which it gave pyroxene and glass. (Table IX.)

The figure used in the discussion (fig. 13) is the experimentally determined figure for 1400°, determined by the temperature method. It shows that the pyroxenes (K to L) are very much richer in magnesia than the liquids with which they are in equilibrium (G to H). As will appear later, this is uniformly true in the present system except in compositions very close to diopside.

The three-phase-boundaries for several other temperatures were determined by this method of finding the temperature of beginning of melting for various mixtures. The procedure is to hold the completely crystallized mixture at successively higher temperatures until the temperature is attained at which the first trace of glass is found in the quenched product. The results are given in Table IV. The information given in Table IV is expressed graphically in figs. 14 and 15, i. e. the three-phase-boundaries are drawn. Only those drawn in full lines have been experimentally determined. It was not possible to fix them accurately for the lower temperatures because over a considerable range of composition these lower-melting mixtures show practically the same temperature of beginning of melting. Dotted lines are given to show the general direction which the undetermined lines must take.

TABLE IV.

Temperature of Beginning of Melting.

Composition*		
Pyroxene	SiO_2	Temperature
$100(Di_{83}En_{17})$	0	1390 ± 4
$100(Di_{75}En_{25})$	0	1390 ± 4
$100(Di_{56}En_{44})$	0	1390 ± 4
$100(Di_{37}En_{63})$	0	1395 ± 4
$100(Di_{19}En_{81})$	0	1416 ± 4
$100(Di_{9\cdot5}En_{90\cdot5})$	0	1450 ± 4
$95(Di_{75}En_{25})$	5	1365 ± 4
$95(Di_{56}En_{44})$	5	1375 ± 4
$95(Di_{19}En_{81})$	5	1400 ± 4

FIG. 14.

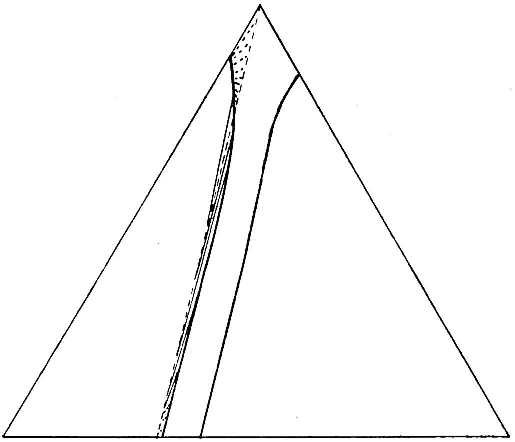


FIG. 14. Showing three-phase-boundaries for the phases pyroxene, forsterite and liquid (true scale).

Fig. 16 is analogous to fig. 13 and shows the relations at various isotherms.

The points *a* and *b* of fig. 16 for 1390° correspond with the points L and K of the theoretical case fig. 12 (*b*).

The Course of Crystallization in Typical Mixtures.

We are now in a position to discuss, with the aid of the three-phase-boundaries, the crystallization of typical mixtures.

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* The material was in each case subjected to preliminary treatment which consisted in converting the mixture to glass and then crystallizing the glass at about 1300°. The reason for this treatment will appear later.

Crystallization when perfect equilibrium obtains will first be considered.

In the case of two substances which form a eutectic, the crystallization of any mixture can be fully described when the two freezing-point curves have been experimentally determined ; or, if the two substances form a complete series of solid solutions like the plagioclase feldspars, the crystallization of any mixture can be described if solidus and liquidus have been experimentally determined. So in the present system the experimental determination of boundary curves, isotherms and three-phase-boundaries makes possible a discussion of the crystallization of any mixture. Such a discussion is not theoretical, but is based directly on the experimental results. It is true that with a charge of a given composition the exact course of crystallization, necessary when complete equilibrium obtains, can not in some cases be experimentally realized because the charge can not be cooled slowly enough, but, by making quenching experiments at various temperatures, any desired stage of the process can be experimentally realized. The discussion of crystallization when perfect equilibrium is attained is important because a very close approach to this behavior would be furnished by a large body of material when very slowly cooled and kept thoroughly mixed.

Fig. 15.

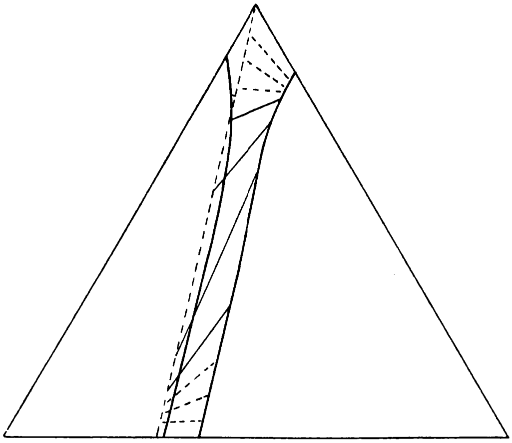
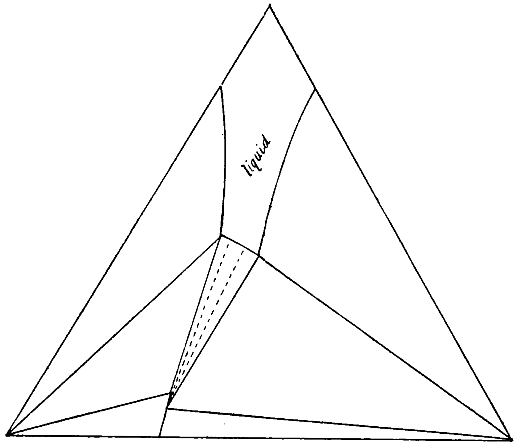


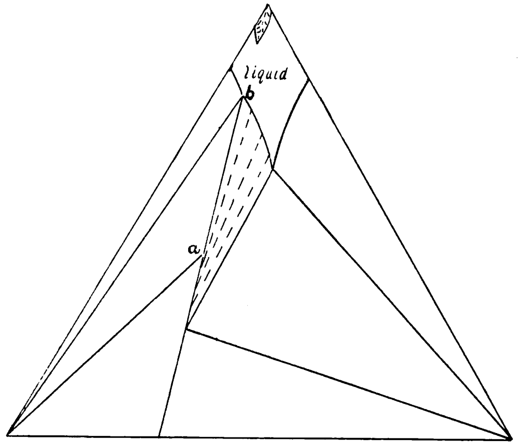
Fig. 15. Showing three-phase-boundaries for the phases pyroxene, silica and liquid (true scale).

In order to make it possible to follow the geometrical relations it is necessary to distort the figure somewhat as has been

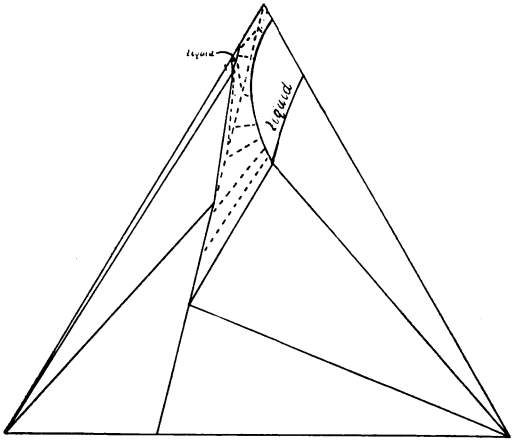
Fig. 16.



1450°



1390°



1388°

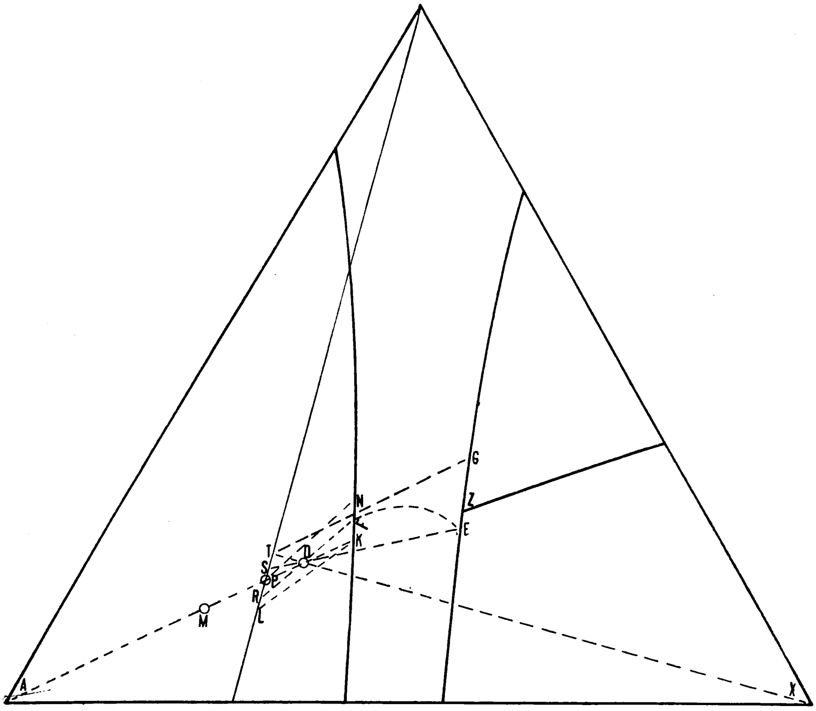
done in fig. 17. The space between the boundary curve, forsterite-pyroxene, and the pyroxene conjugation line, has been widened, relatively, and the three-phase-boundaries, LK, RF, etc., have been made to cross this space less obliquely than they should if drawn to true scale. A glance at figs. 14 and 15 will convince one that the geometrical relations could not be followed if the boundary curves and the three-phase-boundaries were drawn in their proper relative positions. The distorted figure illustrates the principles involved equally well, besides facilitating the discussion.

Crystallization with Perfect Equilibrium between Liquid and Solid Phases.—If a liquid of composition M (fig. 17) is allowed to cool, forsterite begins to crystallize at the temperature of the isotherm through the point M and continues to crystallize until the temperature of the point K on the boundary curve is reached. In the meantime the composition of the liquid has changed from M to K along the straight line AMK. Since liquid K is saturated with pyroxene that phase then begins to crystallize, and since we now pass into a three-phase-area the composition of the pyroxene can be found by drawing the three-phase-boundary through the point K, i. e., KL, and L represents the composition of the pyroxene. When the temperature is further lowered pyroxene continues to crystallize and forsterite begins to redissolve. The composition of the liquid now changes along the boundary curve and the composition of the pyroxene in the act of crystallization, as well as that of the pyroxene which has already separated (if there is perfect equilibrium), changes toward S. When the temperature of the point N is reached, the liquid finally disappears and the whole consists of pyroxene of composition P and forsterite, NP being the three-phase-boundary for the temperature of the point N. The proportion of pyroxene to forsterite is as MA : MP.

If the composition of the original liquid had been that of the pyroxene P, forsterite would crystallize first as before, and the whole course of crystallization would be precisely as given above. At the temperature of the point N, in this case, the last of the liquid and the last of the forsterite are used up simultaneously and the whole consists simply of pyroxene of composition P.

If the composition of the original liquid was that of the point D, forsterite would crystallize first as before and crystallization would follow the same course as in the two preceding cases until the temperature of the point F is reached. At this temperature the last of the forsterite has dissolved and the mixture consists of liquid of composition F and pyroxene of composition R, FR being the three-phase-boundary through the point D. The composition of the liquid now leaves the boundary curve and crosses the pyroxene field on the curve FE, pyroxene continuing to crystallize and changing in composition towards S. When the temperature of the point E is reached cristobalite begins to crystallize. At this temperature the liquid has the composition E and pyroxene the composition S, SE being the three-phase-boundary through the point D for the three phases, pyroxene, cristobalite and liquid. With further lowering of temperature the composition of the liquid changes along the boundary curve from E towards Z, cristobalite and pyroxene continue to crystallize and the pyroxene changes in composition towards T. At the temperature of the point Z cristobalite changes to tridymite, if perfect equilibrium is attained, and with further lowering of temperature tridymite and pyroxene continue to crystallize. When the temperature of the point G is reached the liquid finally disappears; the last minute quantity has the composition G, and the pyroxene has

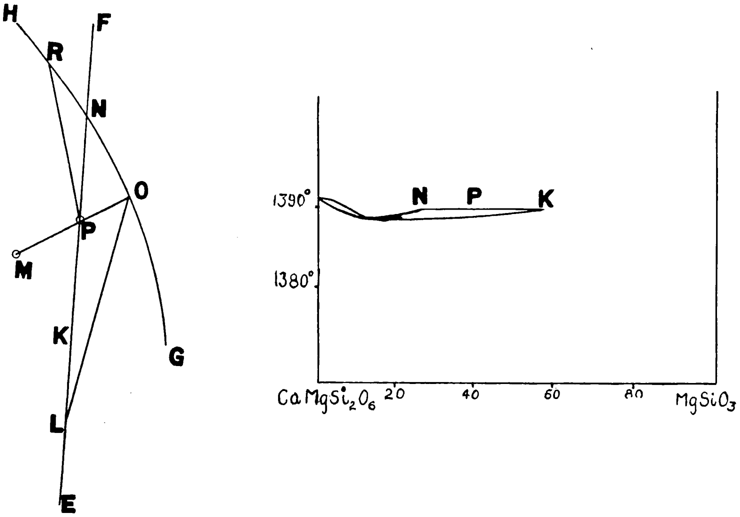
Fig. 17.



the composition T, GT being a three-phase-boundary. The whole now consists of pyroxene of composition T and tridymite in the proportion, pyroxene: tridymite = DX : DT.

It is apparent from the foregoing discussion that all mixtures of forsterite with the pyroxene P become completely crystalline at the temperature of the point N, or, vice versa, begin to melt at the temperature of the point N. The three-phase-boundary PN can, therefore, be determined by taking any mixture of forsterite with pyroxene of composition P, or pyroxene P itself, and determining the temperature of beginning of melting. It will be recalled that this was the method used in determining the three-phase-boundaries.

Fig. 18.



Similarly any mixture of tridymite with the pyroxene T, but not pyroxene T itself, begins to melt at the temperature of the point G and the first minute quantity of liquid formed has the composition G.

In fig. 18 the behavior is represented of mixtures whose composition lies closer to the point at which the boundary-curve, forsterite-pyroxene, cuts the pyroxene conjugation line. FE is a portion of the conjugation line and GNH a portion of the boundary curve. If a liquid of composition M is crystallized, forsterite first separates and the composition of the liquid changes toward O. At the temperature of the point O, pyroxene of composition L begins to crystallize, OL being the three-phase-boundary for the temperature of the point O. The composition of the liquid now follows the boundary curve, forsterite gradually redissolves and pyroxene changes in composition. When the liquid has the composition N the pyroxene has the composition K. When the temperature of the point R is reached, the liquid finally disappears, the vanishing amount having the composition R, and the pyroxene having the composition P, RP being the three-phase-boundary for the temperature of the point R. The whole then consists of forsterite and pyroxene P.

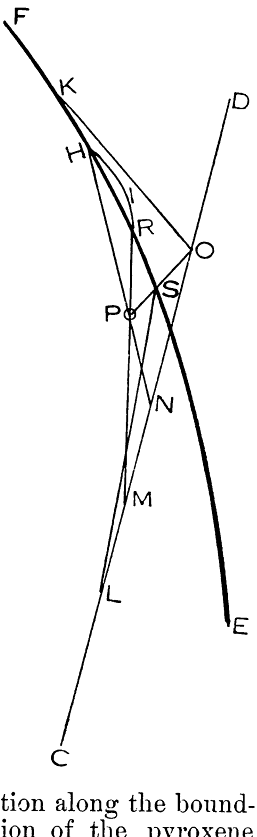
If the original mixture had the composition P, forsterite would separate first, as before; at O, pyroxene L would begin to separate and forsterite to redissolve, the whole behavior being the same as that of composition M, until the temperature of the point N is reached. At this temperature the re-solution of forsterite is complete and the whole consists of pyroxene K and liquid N, which is also of pyroxene composition. Thenceforth the melt behaves as a binary mixture and its behavior is expressed in the simple binary diagram of fig. 18, in which the points N, P and K correspond with the points so lettered in the ternary figure and of which no further explanation is necessary. All the rearrangement between liquid and solid which is necessary in order to get crystallization strictly according to the binary diagram of fig. 18 is, of course, in practice impossible on account of the very small temperature interval involved. What really happens is the crystallization of the liquid N *in toto* to pyroxene of composition N.

The behavior of liquid of composition P is typical of that of all liquids of pyroxene composition between N and K. The behavior of liquids of composition between K and pure $MgSiO_3$ is given in the discussion of the liquid P of fig. 17. All liquids between N and pure diopside behave as binary mixtures and the binary diagram of fig. 18 expresses their behavior completely.

The existence of both the solidus and liquidus shown in fig. 18 is, of course, not experimentally determinable on account of the extremely small intervals involved. All that has been shown is the existence of a very flat minimum, whose exact position cannot be located. The occurrence of the minimum was proved as follows: A charge of a given composition close to diopside was compared with diopside by quenching the two together from the same temperature. The charges were separated only by platinum foil ·02^{mm} thick, so that there was no possibility of a difference of temperature. In this manner it was shown that the composition, diopside 82 per cent, $MgSiO_3$ 18 per cent, and also the mixture 77 per cent diopside give only glass at a temperature slightly lower than that at which the diopside gives only glass. Of these two mixtures the 82 per cent mixture is completely molten at a temperature slightly lower than the 77 per cent mixture. These observations show that there is a minimum in the neighborhood of the 82 per cent mixture, though it is not more than 2°–3° lower than the melting-point of diopside. The occurrence of the minimum is entirely consistent with all the relations found in the system.

The Precipitation, Complete Solution and Reprecipitation of Forsterite.—There is a small area, close to the point of intersection of the boundary curve and conjugation line, every point of which lies at the intersection of two three-phase-boundaries. The point P of fig. 19 represents one of these. The crystallization of a liquid of composition P takes place in the following manner: Forsterite first crystallizes out and the liquid changes in composition towards S. At the temperature of the point S pyroxene of composition L begins to crystallize out. When the temperature is lowered the composition of the liquid follows the boundary curve, forsterite begins to dissolve and the pyroxene to change in composition. When the temperature of the point R is reached, the liquid has the composition R, forsterite has completely redissolved and the pyroxene has the composition M, RM being the three-phase-boundary for the temperature of the point R. The composition of the liquid now leaves the boundary curve and follows the general course RIH lying entirely in the pyroxene field. During the temperature interval between R and H, the mixture consists entirely of pyroxene crystals and liquid, without crystals of forsterite. At the temperature of the point H the pyroxene has the composition N and reprecipitation of forsterite begins, HN being the three-phase-boundary for the temperature of the point H. With further lowering of temperature crystallization of both pyroxene and forsterite continues, the liquid changing in composition along the boundary-curve towards K, and the composition of the pyroxene changing towards O. When the temperature of the point K is reached the liquid finally disappears, the last vanishing quantity

Fig. 19.



having the composition K. The whole then consists of pyroxene O and forsterite (OP produced passes through the composition of forsterite).

In the actual system under investigation the temperature interval between the points S and K is only 2°–3° and the behavior above described cannot be experimentally realized, and, therefore, has no practical importance in the present system. The necessity of such a behavior is, however, important as a general fact in systems of like character inasmuch as it illustrates the possibility of the precipitation, complete solution and reappearance of a crystalline phase as the normal result of cooling.

Crystallization without Interaction between the Liquid and the Solid Phases Already Separated.—The crystallization of any mixture of a system such as the present may be considered to take place in a manner somewhat different from that outlined for the case of perfect equilibrium. It may be considered that when a crystal has separated it is never redissolved and that when a mix-crystal separates its composition does not thereafter suffer any change. The crystals which are separating at any instant are at equilibrium with the liquid but those that have already separated may not be.

When crystallization takes place in this manner a liquid of composition M, P or D of fig. 17 would behave as follows: Forsterite would crystallize out first and the composition of the liquid would change to K. At the temperature of the point K pyroxene of composition L would begin to separate. In the case of complete equilibrium the re-solution of forsterite would now begin and the liquid would change along the boundary curve. In the case we are now considering, liquid and forsterite do not interact and the composition of the liquid crosses the pyroxene field and meets the boundary curve pyroxene-tridymite at a point lower than E, say G.* In the meantime the composition of the pyroxene separating has changed from L to T and there exist in the mixture, pyroxene crystals of all compositions varying from L to T. When the temperature is that of the point G and the composition of liquid is G, tridymite begins to crystallize and the composition of the liquid changes along the boundary curve pyroxene-tridymite. Meantime the composition of the pyroxene separating changes from T towards pure diopside and final crystallization takes place only when the temperature is that of the eutectic diopside-tridymite, when the remaining infinitesimal amount of liquid has the composi-

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* The exact curve which indicates the change in the composition of the liquid is, unlike FE, such that the tangent to it at any point passes through the composition of the pyroxene in equilibrium with liquid of the composition and at the temperature represented by the point.

tion of this eutectic and the crystalline phases separating are tridymite and pure diopside.

It will be recalled that we started with any of the mixtures M, P or D. Any of these mixtures would, then, if crystallized in this manner, consist of forsterite, tridymite, and pyroxene varying in composition from L to pure diopside. The actual amount of pyroxene approaching L in composition would be relatively large; the amount approaching diopside, relatively very small; the amount of pure diopside infinitesimal.

Importance of Distinguishing between the Two Types of Crystallization.

It is of great practical importance in working out such a system to bear in mind the distinction between crystallization of these two types. Crystallization of the first type, viz.: that in which there is perfect equilibrium between the liquid and the solid phases, is favored by very slow cooling during which plenty of time is allowed for interaction between the liquid and the solid phases which have already separated from it. Crystallization of the second type is favored by quick cooling during which the liquid is in equilibrium at any instant only with the solid phases separating at that instant. It is very doubtful if, in practice, the period of cooling could ever be sufficiently prolonged to realize crystallization of the first type. Crystallization of the second type is often, however, very closely approached, if not actually realized, by heating a charge of 20 to 50 grams to the liquid state and then removing it from the furnace and allowing it to cool to room temperature. This is, of course, true only of those mixtures which crystallize readily, that is, those rich in pyroxenes or forsterite; the silica rich mixtures may not crystallize at all with such treatment.

If, then, a mixture of composition P (fig. 17) is heated till completely liquid and then allowed to cool, crystallization taking place freely, the result will be forsterite, tridymite and pyroxene varying from L to diopside.* The mixture P should, however, consist, when completely crystalline, simply of homogeneous pyroxene of composition P. The heterogeneous material prepared by rapid crystallization is not at equilibrium—though it will persist indefinitely—and should not be used to investigate equilibrium whether by the method of quenching or by the method of noting the heat effect of any change recorded by the thermoelement in running a heating curve. The initial mate-

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* In the actual case, owing to undercooling, the composition of the pyroxene varies between somewhat narrower limits. The essential point is that the pyroxene is of variable composition.

rial in any such experiment should itself be at equilibrium. If it is desired, for example, to determine the temperature of beginning of melting of a mixture of composition P, the heterogeneous material prepared by rapid crystallization will be found to begin to melt at the temperature of the eutectic between diopside and tridymite. On the other hand, if the homogeneous pyroxene P is the initial material, melting will not be observed until the temperature of the point N (fig. 17) is reached. Now the behavior of the heterogeneous material can be interpreted after the true equilibrium has been studied throughout the system but the converse is not true, that is, equilibrium in the system can not be determined from the behavior of this heterogeneous material.

It has already been stated that any mixture, say the mixture P, can not in practice be cooled slowly enough to ensure perfect equilibrium between the liquid and the solid phases, and a homogeneous pyroxene P cannot therefore be prepared by slow cooling. Since it is necessary to prepare the homogeneous pyroxene of composition P not only in order to obtain material to use in studying equilibrium, but also to prove the very existence of this pyroxene, some other method of making it must be resorted to. The method is simple and consists in quenching a small charge of composition P, from the liquid state, thereby obtaining a glass, and then crystallizing the glass at a temperature below that of the point N. Similarly the mixture M must be crystallized from glass at a temperature below N, if a mixture to be used in studying equilibrium is desired.

It was in this manner that all the pyroxenes between diopside and clino-enstatite were prepared and the fact of complete solid solution between the two compounds, already indicated by the shape of the fusion surfaces, was thereby demonstrated beyond doubt. The heterogeneous preparations prepared by crystallization during cooling from the liquid state create an entirely false impression as to the extent of solid solution, when examined under the microscope, unless the manner of crystallizing already described is previously suspected. The preparation contains both pyroxene close to clino-enstatite and pyroxene close to diopside and the natural conclusion is that there is only limited solid solution close to each compound.

Confirmation of the above statements concerning the mode of crystallization of the cooling liquid comes from the work of Zinke on the diopside-clino-enstatite series.* The mixtures were crystallized by cooling their melts, and Zinke noted, besides diopside and clino-enstatite, pyroxene of small (and variable) optic axial angle. The small optic axial angle is,

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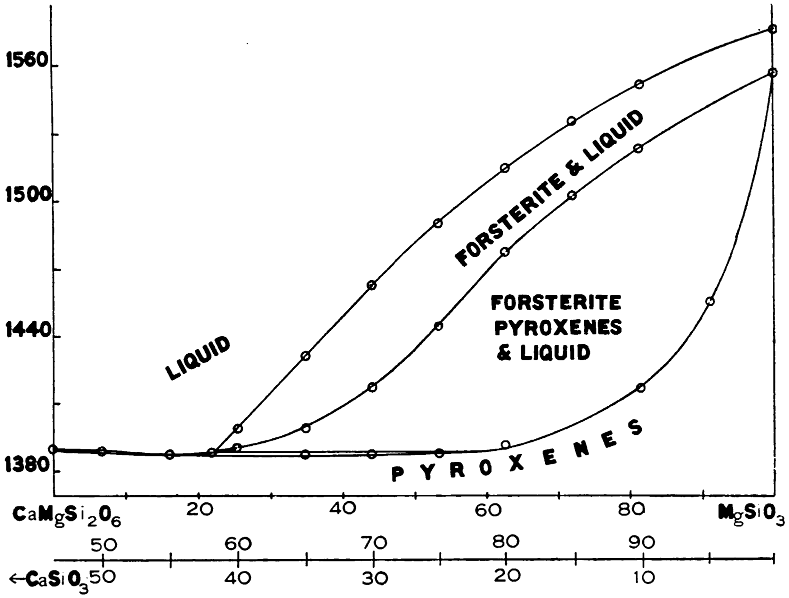
*G. Zinke, Neues Jahrb. Min., 1911, II, p. 132.

as will be shown in the optical part of this paper, characteristic of pyroxenes of intermediate composition. There is no doubt, then, that Zinke obtained intermediate pyroxene of varying composition as we have stated should be obtained with the procedure followed.

It is obvious from the foregoing discussion that in describing any experiment performed on a mixture belonging to such a system it is necessary to state the initial condition of the material used. For nearly all mixtures it is necessary to use material prepared by crystallizing a glass at a low temperature. Any composition lying in the area AEF (fig. 5) including the pyroxene mixtures E to F can, however, be crystallized to an 'equilibrium mixture' simply by cooling from the liquid condition.

Fig. 20.



The Pyroxenes, Diopside-Clino-enstatite.

By using the results of the ternary system a diagram may be constructed for the pyroxenes which exhibits their behavior with change of temperature in a more striking manner than does the triangular diagram where temperature can be represented only by means of isotherms. Such a diagram is shown in fig. 20. Thus the behavior of composition Di_{19} En_{81} is shown in the figure to be as follows: at 1552° forsterite crystallizes out and continues to crystallize down to 1523°. At this temperature pyroxene begins to crystallize out, and until the temperature 1420° is reached, the three phases forsterite, pyroxene and liquid co-exist. At 1420° both forsterite and liquid have disappeared and the whole consists of pyroxene. The diagram, then, expresses the *nature* of the phases present at any temperature in any mixture of given *total composition*. It does not, however, express the *composition* of the individual phases present in a heterogeneous mixture, inasmuch as this can be done only in terms of three components. It records the temperature at which any phase appears or disappears in a mixture of given total composition and therefore indicates the temperature at which a heat-effect takes place in that mixture, or, in other words, the temperature at which a heating-curve break is to be expected. It has been demonstrated that the true ternary equilibrium diagram, when boundary curves, isotherms and three-phase-boundaries are shown, also expresses these facts and has the advantage that it expresses the composition of the phases present at any temperature as well, but the ternary diagram is more difficult of rapid interpretation.

Comparison of the Present Results with Earlier Work.

The system $CaSiO_3$–$MgSiO_3$ had been formerly studied at this laboratory, the method of attack being principally the method of heating curves. The heat-effects indicated by the heating-curve breaks are usually quite adequate for the correct interpretation of equilibrium in the system, but it happened that in the present case they were not. The difference between the conclusions arrived at in the early work and those arrived at after making quenching experiments is the result of two factors. In the first place the heating-curve method is likely to overlook a change involving a small heat-effect when this change occurs at a temperature only a little higher than another involving a considerable heat-effect. The large effect at the lower point may completely mask the smaller effect which should be obtained at the higher point. It is true that by special treatment the higher point can often be fixed, in such cases, by the method of heating curves, but the fact remains that the existence of the higher point may not even be suspected and the special treatment not applied. Heating-curve results are, then, likely to err in the direction of incompleteness.

In the second place, even when all heating-curve breaks have been obtained, it is not always easy to decide what the nature of the changes which have given the breaks may be. It is always possible that the materials on which a heating-curve is run is not itself an equilibrium mixture and the temperatures at which breaks occur are therefore, possibly, not the temperatures of equilibrium changes. When the attempt is then made to decide what change of phase has taken place at the temperatures of the breaks, the conclusions may be erroneous.

With the method of quenching, however, when supplemented by microscopic examination of the product, there is no room for doubt as to the nature of the phases present at equilibrium and the temperatures of all changes can be definitely fixed, even when there are two, or even more, at temperatures little removed from each other, and whatever may be the relative values of the heat-effects involved. The treatment can, moreover, always be made such that both the material started with and the final product represent equilibrium.

The above statements are not intended as an argument for the general superiority of the quenching method over the method of heating curves. The existence of a promptly reversible change, such as the inversion α–β quartz, can be easily missed when the quenching method is employed but may be readily detected by the method of heating curves. No fault can be found with the accuracy of the heating-curve break itself, but there is some danger of misinterpreting the breaks when the method is employed by itself in the study of equilibrium in a complex system.

Both the factors mentioned, viz.: the overlooking of certain changes and the obtaining of breaks which do not represent equilibrium changes, are involved in the results of the earlier work on the system $CaSiO_3$–$MgSiO_3$.

The material on which the heating-curves were made was prepared in most cases by cooling a mixture from a temperature at which it was liquid to room temperature, crystallization taking place freely. It has been shown, in the discussion of the course of crystallization, that, when mixtures are allowed to crystallize in this manner, the resultant product consists, for the more calcic mixtures, 100–75 per cent diopside, of homogeneous pyroxene. By virtue of undercooling, somewhat more magnesian mixtures, extending perhaps as far as 65 per cent diopside, may also consist of homogeneous pyroxene if the cooling has been at the proper rate. In the earlier work, therefore, on finding that all mixtures extending from diopside to $Di_{65}En_{35}$ gave a homogeneous product it was concluded that solid solution extended as far as $Di_{65}En_{35}$.

The more magnesian preparations, however, crystallize to a mixture of forsterite, pyroxene of variable composition and free silica. Since the microscope showed inhomogeneity, and since the forsterite was not recognized as such, but was considered to be the high-temperature form of $MgSiO_3$ (α-$MgSiO_3$), these mixtures were considered to lie beyond the limits of solid solution.*

The thermal results obtained seemed to be in accord with these conclusions, for these more magnesian preparations gave two heating-curve breaks, one of which appeared to be interpretable as the result of inversion of β-$MgSiO_3$ to α-$MgSiO_3$ and the other, as the result of eutectic-melting between $MgSiO_3$ and diopside solid solution.

The heating-curve breaks obtained on the more calcic mixtures (those that crystallized to homogeneous pyroxenes) should indicate the temperature of equilibrium changes and should therefore agree with the quenching results. This they do. Heating-curve results obtained on the more magnesian, inhomogeneous material, not itself at equilibrium, may indicate other changes. The completed results of the ternary system make it possible, however, to state what effects should be observed in this inhomogeneous material.

Since the material contains free silica and medium-calcic pyroxene there should be a notable melting-together of these two at temperatures corresponding to the flat portion of the boundary curve tridymite-pyroxenes (1370°-1380°; see fig. 7). Since forsterite is present also there should be melting of it with a further quantity of pyroxene at temperatures corresponding to the flat portion of the boundary curve pyroxene-forsterite (1387°-1389°). The melting should in each case give a heating-curve break and it was approximately at these temperatures that breaks were obtained in the earlier work. As already pointed out, the lower of these two breaks was at that time considered probably due to inversion in $MgSiO_3$, but this involved the difficulty that the break could not be obtained in $MgSiO_3$ itself. It has been shown by Bowen and Andersen that this suspected inversion in $MgSiO_3$ has no real existence inasmuch as the material called α-$MgSiO_3$ has proven to be forsterite Mg_2SiO_4. The break cannot, therefore, be the result of inversion. The presence of the break in all mixtures containing lime and its absence in pure $MgSiO_3$ is, however, in direct accord with the conclusion, stated above, that the break is due to the melting-together of silica and medium-calcic pyroxene. If either silica or calcic-pyroxene is absent the

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* The amount of silica is very small (2-3 per cent). It occurs in exceedingly minute particles speckled through some of the other crystals, the effect being merely to impart a dusty appearance to these crystals. It is to be noted that these minute inclusions were observed to be "more numerous in the mixtures which are rich in magnesia (70-97 per cent)."

break must disappear. In $MgSiO_3$ mixtures, therefore, even if crystallized in such a manner that they contain free silica, the break should not occur, since there can be no calcic pyroxene present.

In the earlier work it was noted that when the intermediate mixtures were crystallized from glass at a low temperature and a heating curve run on such material the lower break was not obtained. Preparations crystallized in this manner consist of homogeneous pyroxene. There is no silica and, therefore, the lower break is absent. It is clear that in the absence of either silica or medium-calcic pyroxene this lower break disappears, in fact, it must be absent in all mixtures of $CaMgSi_2O_6$ and $MgSiO_3$ when the preparation started with is an equilibrium mixture, i. e. homogeneous pyroxene.

Figure 20 shows that not only should the lower of these two breaks be absent in *all* pyroxene mixtures but the higher one, termed the eutectic in the earlier work, should also disappear in the more magnesian mixtures, 58-100 per cent $MgSiO_3$, when they are crystallized in such a manner that they consist of homogeneous pyroxene. The finding of the higher break in the more magnesian mixtures is the direct result of the fact that the preparations were crystallized in such a manner that they consisted of forsterite, pyroxene of various compositions and free silica. The melting-together of pyroxene and forsterite gave the break.

In order to compare directly the behavior of homogeneous material and of inhomogeneous material of the above kind I have made quenchings of the two side by side, taking the mixture diopside 63 per cent. The quite different behavior of the two is displayed in the table below:

Temp.	Homogeneous	Inhomogeneous
1382°	no change	stringers of glass formed
1390°	no change	increased amount of glass
1398°	beginning of melting minute amount of glass	30–40 per cent glass

I have also run heating-curves on the mixture En_{81} Di_{19}. Homogeneous material, made by crystallizing the glass, gave no breaks at these lower points, whereas material crystallized by cooling the liquid gave a distinct break at 1372° owing to the presence of free silica.

In the earlier work a series of breaks recorded as the "upper points" (Table II, p. 8) were obtained in the more magnesian mixtures. These temperatures correspond very closely with the temperatures, located by quenching, at which the last of the pyroxene disappears (dissolves), leaving liquid and forsterite. The degree of correspondence is shown in Table V, columns II and III.

TABLE V.

I %$MgSiO_3$	II Heating curve break "Upper Point"	III Final disappearance of pyroxene determined by quenching	IV Final disappearance of forsterite determined by quenching
72†	1424*	1425	1474
73	1427	1430	1484
75	1432	1440	1490
80	1474	1477	1515
90	1524	1523	1552
95	1543	1543	1558
100	1557	1557	1577

* The figures given in column II are the values found in the earlier work corrected in terms of the extended gas-thermometer scale, see Day and Sosman: The Melting Points of Minerals in the Light of Recent Researches on the Gas Thermometer, this Journal (4), xxxi, 341–349, 1911.

† The figures in column I are in terms of the components $CaSiO_3$ and $MgSiO_3$; see lower scale of figure 20.

A still higher break corresponding to the temperature at which forsterite finally disappears in the liquid was not obtained in the earlier work and it has remained for quenching to determine the existence and the limits of the temperature interval during which the various mixtures consist of forsterite and liquid (see Table V and figure 20).

Summary of Comparison of Results.—The comparison of the results of the earlier and the present work may now be summarized. The method of heating-curves was employed in the earlier work and the mixtures were crystallized in such a manner that some of them consisted of pyroxene of variable composition, forsterite and silica, and were not equilibrium mixtures. On this material two breaks were obtained, near each other, at about 1375° and 1385°. The lower break, formerly attributed to inversion, has been found by quenching to be due to the melting-together of silica and pyroxene and the higher break to the melting-together of forsterite and pyroxene. No change occurs at the temperature of the lower break in any mixture when the material started with is homogeneous pyroxene, as it should be at equilibrium. No change occurs at the temperature of the higher of these two breaks in the more magnesian mixtures when they consist of similar homogeneous material. The temperature recorded as the upper point in the earlier work corresponds with the temperature of final disappearance (solution) of pyroxene, leaving liquid and forsterite. The existence of a temperature interval during which the mixture consists of forsterite and liquid was overlooked in the earlier work but revealed by quenching.

OPTICAL STUDY

Throughout the investigation the products of the various operations were examined under the microscope in order to identify the phases present. In the ordinary course of the work it was necessary to observe only a sufficient number of the properties of any phase to make its identification certain, but, whenever specially suitable material was obtained, determinations of all the measurable optical properties were made. In the following the values found for the various phases are recorded.

Forsterite.

The properties of pure forsterite have been given in former publications from this laboratory and will simply be listed here without discussion.

Crystal system–orthorhombic ; $a : b : c = 0{\cdot}463 : 1 : 0{\cdot}584$
Cleavage 010, 001 distinct. $G = 3{\cdot}216$
Refractive indices, $\gamma = 1{\cdot}670_4$ $\beta = 1{\cdot}651_0$ $\alpha = 1{\cdot}635_1$
$\gamma - \alpha = {\cdot}035_3$ $2V_{Na} = 85°16'$. Orientation $c = \mathfrak{b}$ and $a = \mathfrak{c} = Bx_a$

Cristobalite and Tridymite.

Silica was found in the form of cristobalite in mixtures quenched from 1500° or higher and as tridymite in those quenched from about 1400° or lower. At intermediate temperatures it was usually possible to prove that both were present. These observations are in accord with Fenner's conclusion that tridymite and cristobalite are enantiotropic and the inversion point about 1470°, the change being decidedly sluggish.*

Cristobalite occurred in the glass sometimes as sharply outlined octahedra, slightly modified by the cube. The cube was, however, usually the more prominent form and, by distortion, the crystals usually appeared as stout prisms. The double refraction was barely discernible with the aid of the sensitive tint plate.

Tridymite was in the form of broad thin plates which appeared as needles when turned on edge. The needle-shaped sections had quite marked double refraction, parallel extinction and negative elongation.

The Diopside-Clino-enstatite Series of Pyroxenes.

The compounds $MgSiO_3$ and $CaMgSi_2O_6$ form a complete series of mix-crystals or solid solutions, crystallizing in forms corresponding with monoclinic pyroxenes. The existence of

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* Fenner, C. N.: The Stability Relations of the Silica Minerals, this Journal (4), xxxvi, 337, 1913.

complete solid solution is proved by the fact that any mixture between the two can be crystallized to a homogeneous crystalline mass which shows only the one kind of crystals. Complete solid solution is again proved, though further proof is unnecessary, by the character of the fusion surfaces found for the ternary system, i. e. the absence of any quintuple point (point at which liquid and three solid phases are in equilibrium). Moreover, any member of the series can be obtained in contact with liquid in the ternary system.

In order to prepare a pyroxene of a given composition, a mixture of the desired composition is converted to a glass, by quenching it from the liquid state, and the glass is then crystallized by heating at a temperature of from 1300° to 1350°. The heating is best prolonged for several days in order to increase the grain of the crystalline aggregate. The reasons for this procedure have already been stated in detail; suffice it to repeat here that, if the mixture is crystallized simply by allowing it to cool from the liquid state, the result is, for the more magnesian mixtures, pyroxene of variable composition (zoned pyroxene), forsterite and silica. The precaution is unnecessary in the more calcic mixtures, those containing up to about 35 per cent $MgSiO_3$, 65 per cent $CaMgSi_2O_6$, for these do crystallize to homogeneous pyroxene if cooled quickly from the liquid state.

In the earlier work on these mixtures the material submitted to microscopic examination was crystallized simply by cooling the liquid and the result stated above was found—all mixtures as far as about 35 per cent $MgSiO_3$, 65 per cent $CaMgSi_2O_6$ were found to consist of homogeneous pyroxene. The properties of these pyroxenes were carefully determined by Wright and Larsen and found to vary continuously with composition. In the present work it has been possible to show, by crystallizing from glass, that this continuous variation of properties does not cease with the 35 per cent $MgSiO_3$ mixture, but extends as far as the pure $MgSiO_3$ itself. The properties found for the pyroxenes as far as the 35 per cent $MgSiO_3$ composition agree precisely with those found by Wright and Larsen.*

Twinning.—The variation in the tendency to form twinned crystals appears to be continuous, though it is, of course, a property which does not admit of quantitative measurement. The twinning is always after 100. In pure clino-enstatite every grain when turned into the proper position shows narrow twinning lamellæ. In 80 per cent $MgSiO_3$, 20 per cent $CaMgSi_2O_6$ the same is true, but the twinning lamellæ have a distinct tendency towards a greater average width. In 60 per cent $MgSiO_3$, 40 per cent $CaMgSi_2O_6$ the breadth of the lamellæ is still greater; many of the grains show only two twinning

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*This Journal (4), xxvii, p. 38, 1909.

bands, though most of them are polysynthetically twinned. In 45 per cent $MgSiO_3$, 55 per cent $CaMgSi_2O_6$ most of the grains are twinned only twice though many show several lamellæ. Closer to diopside the twinning is distinctly less frequent. In diopside itself most of the grains are untwinned, several show two twinned bands and only rarely is repeated twinning observed. This progressive increase in the tendency towards twinning was observed in mixtures crystallized by heating various glasses under the same conditions. It will be shown later that in the same pyroxene the tendency towards twinning varies when it is formed by different methods.

Extinction Angle.—The extinction angle on 010 can be measured very closely and shows the continuous variation in an excellent manner. The angle was found by measuring symmetrical extinctions against the trace of the twinning plane in those grains which showed this trace and the prismatic cleavage parallel to each other. By choosing such grains, a section in the prism zone was ensured and by choosing those in which there was no overlapping of the twinning lamellæ a section close to the clino-pinacoid was obtained. The overlapping of the twinning lamellæ is an especially delicate test in the present case because the lamellæ are usually much narrower than the thickness of the grain and a very slight turning from the clino-pinacoidal section gives a marked overlapping. For each pyroxene, measurements were made on ten or more grains and several measurements on each grain. An example is given below of the symmetrical extinctions found on different grains of composition $CaMgSi_2O_6$ 37 per cent, $MgSiO_3$ 63 per cent.

$$c \wedge \mathfrak{c} = \begin{matrix}30\\29\end{matrix}\quad\begin{matrix}31\\30\end{matrix}\quad\left\{\begin{matrix}27\\33\end{matrix}\right\}\quad\begin{matrix}32\\29\end{matrix}\quad\begin{matrix}31\\30\end{matrix}\quad\begin{matrix}30\\30\end{matrix}\quad\begin{matrix}29\\28\end{matrix}\quad\begin{matrix}30\\30\end{matrix}\quad\begin{matrix}30\\30\end{matrix}\quad\left\{\begin{matrix}30\\34\end{matrix}\right\}\quad\left\{\begin{matrix}27\\29\end{matrix}\right\}\quad\begin{matrix}31\\30\end{matrix}$$

mean, after rejecting those pairs that are somewhat unsymmetrical (in brackets) = 30°.

Some compositions did not give quite as accordant results as the above. The measurements on $CaMgSi_2O_6$ 56 per cent–$MgSiO_3$ 44 per cent were, for example, as follows:

$$c \wedge \mathfrak{c} = \left\{\begin{matrix}31\\37\end{matrix}\right\}\quad\left\{\begin{matrix}40\\27\end{matrix}\right\}\quad\begin{matrix}32\\36\end{matrix}\quad\begin{matrix}34\\34\end{matrix}\quad\begin{matrix}35\\34\end{matrix}\quad\begin{matrix}33\\36\end{matrix}\quad\left\{\begin{matrix}31\\39\end{matrix}\right\}\quad\begin{matrix}31\\35\end{matrix}\quad\begin{matrix}34\\35\end{matrix}\quad\begin{matrix}34\\34\end{matrix}\quad\begin{matrix}35\\33\end{matrix}\quad\begin{matrix}31\\37\end{matrix}\quad\begin{matrix}32\\36\end{matrix}$$

mean = 34°.

The angle $c \wedge \mathfrak{c}$ for other compositions was found to be as given below in Table VI.

The curve indicating the change of extinction angle with composition (fig. 21) is convex upwards, that is, the angle increases more rapidly near the clino-enstatite end of the series.

TABLE VI.

Composition		Extinction Angle $c \wedge c$ on 010
$MgSiO_3$	100 %	22°
"	81 %	26°
"	63 %	30°
"	53·5%	31·5°
"	44 %	34°
"	25·5%	36°
"	7·0%	37·5°
Diopside		38·5°

FIG. 21.

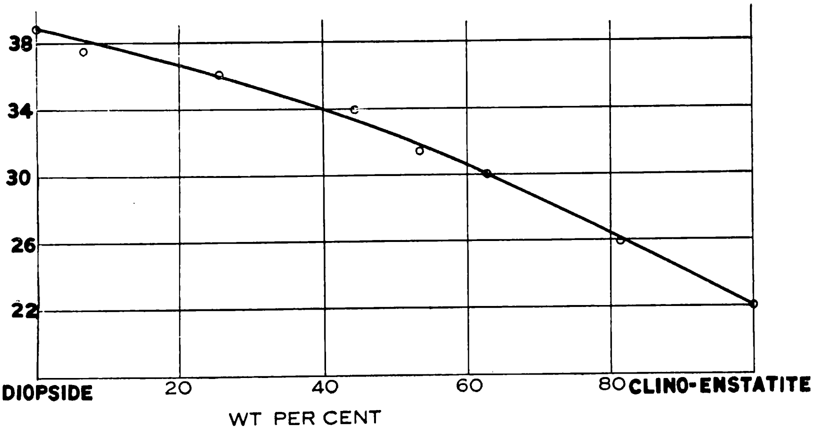

FIG. 21. Extinction Angles of Pyroxene Series.

FIG. 22.

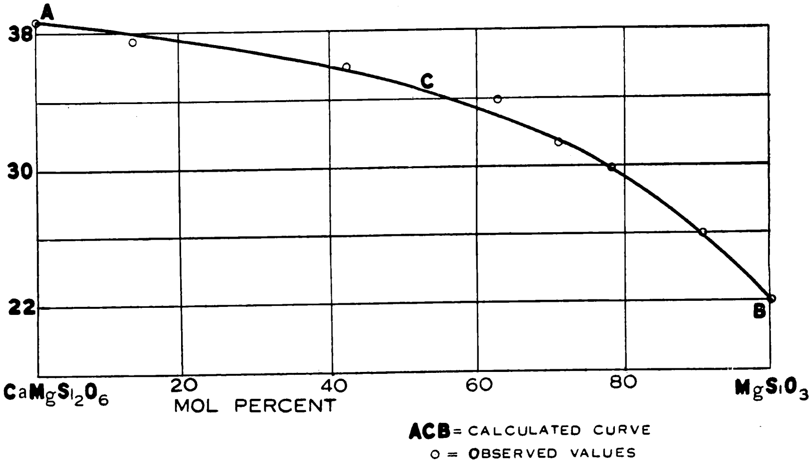

FIG. 22. Extinction Angles of Pyroxene Series.

If it is assumed that the molecular weight of clino-enstatite is the formula weight, $MgSiO_3$ = 100·6, and that of diopside also the formula weight, $CaMgSi_2O_6$ = 216·37, and the composition is plotted in mol. per cent, then the measured values of the extinction angles agree closely with the values calculated by means of Mallard's formula.* In fig. 22 the circles indicate the measured values of the extinction angles plotted in this manner and the curve ACB is calculated from the Mallard equation. The equation reads

Fig. 23.

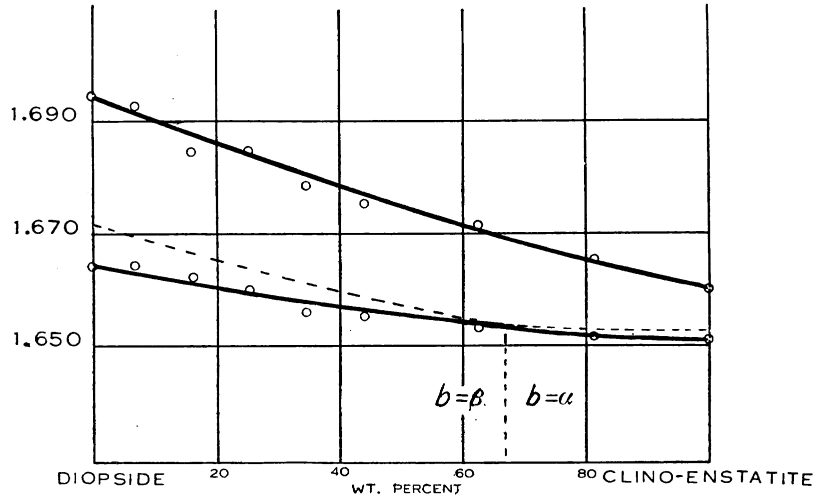

Fig. 23. Refractive Indices of Pyroxene Series.

$$\operatorname{cotg} 2a = \frac{n_1 d_1}{n_2 d_2} \cdot \frac{1}{\sin 2(i_1 - i_2)} + \operatorname{cotg} 2(i_1 - i_2)$$

where $(i_1\text{-}a)$ is the desired extinction angle of a pyroxene mix-crystal containing n_1 mols diopside to n_2 mols clino-enstatite; d_1 and d_2 the birefringence of diopside and clino-enstatite respectively, and i_1 and i_2 their extinction angles.

The agreement of the observed points with the calculated curve is marked. It may be purely accidental, indeed the assumption that the molecular weight is equal to the formula weight for each of the compounds may be quite unwarranted, for if a near-equality of molecular volumes is necessary for complete solid-solution, the molecular weight of clino-enstatite

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* Bull. Soc. Min., iv, 101, 1881.

would have to be twice the formula weight in order to make the molecular volumes nearly equal and give likelihood of solid solution, but it is by no means certain that this similarity of molecular volumes is necessary. At any rate, the agreement seems worth recording.

Refractive Indices.—The refractive indices of the pyroxenes formed by crystallizing the glass were determined by matching with liquids in sodium light and then determining the refractive index of the liquid on the total refractometer. Only the maximum and minimum indices γ and α can be determined by this method. The measured values of γ and α are given in Table VII and are plotted in fig. 23. The average probable error of the values is ±·002, though the accuracy is usually somewhat better in the compositions with low birefringence and occasionally not so good in those with higher birefringence.

TABLE VII.

Composition			
Diopside	Clino-enstatite	γ	α
100	...	1·694	1·664
92	8	1·692	1·664
84	16	1·684	1·662
75	25	1·684	1·660
65	35	1·678	1·655
56	44	1·675	1·655
37	63	1·671	1·653
19	81	1·665	1·651
..	100	1·660	1·651

Optic Axial Angle.—The optic axial angle of various members of the series was measured on grains under the microscope. Sections showing the emergence of one axis were used for those having a large angle, but for a considerable range of compositions the angle is sufficiently small that sections showing the emergence of both axes were available. The material formed by crystallizing the glass at a low temperature was not entirely satisfactory for this purpose in compositions towards the magnesian end of the series, on account of the increasing prevalence of polysynthetic twinning towards that end. It was possible to prove, however, with this material, that the optic axial angle, beginning from the diopside end, grows smaller. In $MgSiO_3$ 63 per cent, diopside 37 per cent the angle is very small and the plane of the optic axes, as in all the more calcic members, is //010, normal to the twinning plane. In $MgSiO_3$ 81 per cent, diopside 19 per cent the angle is again small, but the plane of the optic axes is normal to 010 and parallel to the trace of the twinning plane.

It is evident that in some composition between these two, the value of the optic axial angle passes through zero. In order to study more closely this change in the plane of the optic axes, it was desirable to prepare crystals of known composition, in which the width of the individual twinning lamellæ was greater than in material prepared by crystallizing glass of the pyroxene composition. It has already been shown that, when the three-phase-boundaries for the ternary system have been determined by the method of finding the temperature of beginning of melting of various mixtures (temperature method), a mixture can be chosen which, when held at a certain temperature, will give liquid, pyroxene of a certain composition and another crystalline phase. Thus a mixture of known composition can be chosen, held at a measured temperature and the composition of the crystals of pyroxene to be obtained can be predicted. It is not necessary, however, to depend on the prediction, for the composition of the pyroxene can be determined by measuring symmetrical extinctions on 010. A check is thereby obtained on the prediction and therefore, ultimately, on the determination of the three-phase-boundaries by the temperature method. The prediction is, therefore, an unnecessary part of the process, though very desirable since it removes the necessity of a number of trials.

When pyroxene crystals, embedded in glass, are prepared by this method it is found that the width of the individual twinning lamellæ is greater than in the same pyroxene prepared by the other method, It is, therefore, much less of a task to find a crystal which will give a good interference figure and a dependable value for the optic axial angle. In practice it is necessary to start with a mixture of suitable composition, *in the form of glass*, and to raise the glass quickly to the desired temperature. Mixtures containing a moderate excess of silica above pyroxene composition are more suitable than others, for, during the time necessary to raise the temperature to the desired point (2 or 3 minutes), no crystallization takes place in these somewhat viscous mixtures. All crystallization takes place, therefore, at the desired point, during the time the charge is held there, and it is thereby insured that all the pyroxene has the composition appropriate to this temperature. With less viscous, less siliceous mixtures, the charge cannot be raised to the desired temperature quickly enough to prevent some crystallization *en route*. Any pyroxene formed at a lower temperature will not have the desired composition and, once formed, it is very difficult to get rid of, for later crystallization is likely to take place about these early crystals. It is, of course, even more undesirable to start with material already crystallized. In such a case it is often plainly discernible that the resultant pyroxene crystals have a different composition in their inner and outer portions.

It was desirable to resort to this method of growing the pyroxene crystals in a liquid, only in the case of the more magnesian pyroxenes, thereby to increase the width of the twinned bands and to facilitate optic axial angle measurements. The width of the bands is sufficiently great in the more calcic members, when formed by crystallizing glass of the composition of the desired pyroxene. The composition of the pyroxene is, of course, known absolutely, when prepared by the latter method. When prepared by growing the crystal in liquid the composition is known only as closely as it can be determined from extinction angle measurements (within 5 per cent $MgSiO_3$). Other things being equal, the material whose composition is certain is preferable, but, for the purpose of studying the change in the plane of the optic axes, the crystals whose composition is known only approximately have the advantage already pointed out.

Pyroxenes prepared by either one of these methods could hardly be termed excellent material for optic axial angle measurement, but fortunately the change of angle is very great and the fact of continuous variation between the two end members readily fixed.

TABLE VIII.

Pyroxene Prepared by Crystallization of Glass.

Composition			
Diopside	Clino-enstatite	Plane of Optic Axes	2 V
100	...	//010	59° ± 3°
75	25	//010	56° ± 3°
65	35	//010	47° ± 6°
56	44	//010	40° ± 6°
37	63	//010	very small
19	81	⊥010	20° ± 6°
...	100	⊥010	53° ± 3°

The composition of the pyroxene, which for monochromatic light is uniaxial, was placed between diopside 37 per cent and diopside 19 per cent by using pyroxenes crystallized from glass (Table VIII). By using pyroxene grown in a liquid (Table IX) it was placed within the narrow limits, diopside 35 per cent and diopside 30 per cent.

In figure 23 the refractive indices for the various compositions, as shown in Table VII, are plotted. The values for β are calculated approximately from the above determinations of

TABLE IX.

Pyroxene Prepared by Growing in Liquid.*

I	II	III	IV	V	VI
Total Composition of Charge	Temperature	c ∧ c of pyroxene	Composition of pyroxene from III, % diopside	2 V	Plane of optic axes
(Di 56 En 44) 97% SiO_2 3%	1375°	33·5°	54	40° ± 3°	//010
“ “ “ “	1385°	31·0°	41	20° ± 3°	//010
“ “ “ “	1392°	29·7°	35	10° ± 3°	//010
“ “ “ “	1400°	28·5°	30	15° ± 3°	⊥010
(Di 37 En 63) 95% SiO_2 5%	1410°	25·5°	17	25° ± 3°	⊥010

the optic axial angle. The curve for β is given because it presents graphically the reason for the observed behavior of the optic axial angle, the reason being, of course, that the values of β and α converge, become equal and then again diverge. A change from $b = \beta$ to $b = \alpha$ necessarily takes place at the composition of the uniaxial pyroxene.

Summary of Optical Properties of Pyroxene Series.—The optical properties of the series of pyroxenes, diopside-clinoenstatite, may now be summarized briefly. With increasing $MgSiO_3$ the extinction angle decreases continuously from 38·5° to 22°, the mean refractive index falls from 1·676 to 1·654, the birefraction decreases from ·030 to ·009 and the optic axial angle, in the plane //010, grows smaller, passes through zero and opens again in the plane ⊥010.

The decreasing optic axial angle, refractive indices, birefringence and extinction angle were all observed by Wright and Larsen on those pyroxenes which were prepared formerly at this laboratory, namely those extending from diopside to about diopside 65 per cent, clino-enstatite 35 per cent.† In the present work these changes have been followed beyond this limit, in fact, to clino-enstatite itself.

G. Zinke,‡ in an investigation of the system, diopside–$MgSiO_3$, noted pyroxenes of small optic axial angle in some of his products. He also found, for one of these, an extinction angle of 32°. The pyroxenes observed by Zinke were, no doubt, some of the intermediate pyroxenes of the series, for the optical properties noted are those which the present

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* In each case the initial material was glass and the time of holding at the given temperature 2 hours.

† Allen, White, Wright and Larsen, this Journal (4), xxvii, 38, 1909.

‡ Neues Jahrb. fur Min. 1911, Bd. II, p. 132.

investigation has shown to be characteristic of the intermediate pyroxenes.

Natural Pyroxenes with Analogous Optical Relations.—In the ordinary text-book descriptions of the pyroxenes there is commonly no mention of a series analogous to the pyroxenes prepared in the course of the present work. Occasionally, however, there is mention of pyroxenes poor in lime which show certain similarities with the magnesia-rich artificial varieties.* In 1906 Wahl made a systematic study of such pyroxenes from a number of localities. Wahl's studies, both optical and chemical, show that there are natural, magnesia-rich, monoclinic pyroxenes and they appear to form a series closely similar to the diopside-clino-enstatite series. Wahl terms those described by him, enstatite-augites.† The natural minerals contain considerable iron and, therefore, differ from the iron-free varieties in many of their properties, but they show the same behavior of the optic axial angle, viz., in the varieties relatively poor in magnesia the axial plane is //010 and the axial angle large; with increasing magnesia, as in the artificial varieties, the angle grows smaller, passes through zero and opens again in the plane normal to 010. Wahl was able to show that the axial angle for blue light passed through zero before that for red light in the ferriferous varieties (p. 39), an observation which the present writer was unable to duplicate in the non-ferriferous pyroxene on account of the extremely small dispersion. Wahl found moreover, that as the axial-angle decreased (magnesia increased) the extinction angle also decreased (p. 33).

The Relation of Clino-enstatite to Enstatite.

It was no part of the plan of the present work to study the relation between clino-enstatite and enstatite, but some of the results obtained have a bearing on the problem and seem worthy of attention.

It has been demonstrated by Wright, Wahl and others that clino-enstatite is monoclinic in symmetry. In all other properties it is very similar to enstatite. The universal prevalence of twinning //100 in clino-enstatite has led Zambonini and others to conclude that enstatite is clino-enstatite in which the twinning is sub-microscopic; that the relation is one of polysymmetry. Some of those who support this view have pointed out that in meteorites and artificial melts clino-enstatite is found, in terrestrial rocks, almost universally, enstatite, and they have considered that the determining factor is the rate of cooling.

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* Cf. Pigeonite-Winchell, Optical Mineralogy, p. 331.

† Die Enstatitaugite, T. M. P. M. xxvi, 1-131, 1907.

According to this view, then, quick cooling, such as occurs in meteorites and artificial melts, gives coarse twinning which is visible under the microscope, whereas relatively slow cooling, as in terrestrial rocks, gives fine, sub-microscopic twinning. During the course of the present work it has been found that quick and slow cooling have precisely the opposite effects, at least, for these pyroxenes. When the crystals form instantaneously from an under-cooled liquid the twinning is very fine; when they are grown by holding for a couple of hours in contact with liquid the twinning bands are broad. It seems extremely unlikely, then, that the crystals of enstatite of terrestrial rocks, which undoubtedly grew in contact with liquid for a considerable period, would have twinning bands so fine as to escape observation. If twinning were present in crystals formed under these conditions the twinning bands would be broad and their presence unmistakable. The fact that no twinning bands are discernible leads the writer to believe that natural enstatite crystals cannot be identical with clino-enstatite and that the relation is not merely one of polysymmetry.

A further indication that enstatite and clino-enstatite should be considered different allotropic forms is, of course, the fact that clino-enstatite and diopside form a complete series of solid solutions, whereas natural minerals point to limited solid solutions between diopside and enstatite.

It should be noted, moreover, that no orthorhombic pyroxene corresponding with enstatite ever crystallizes from any of the mixtures here studied, when they are crystallized by cooling from the liquid state. The writer believes that the so-called enstatite, often described as occurring in products formed by treating like mixtures in this manner, is really forsterite, for forsterite should be present and its presence is not noted.

BEARING OF THE RESULTS ON PETROLOGIC PROBLEMS.

The Series of Lime-Magnesia Pyroxenes.

The experimental work described throws some light on the physico-chemical meaning of zoned pyroxenes. In the mixtures dealt with, such zoning sometimes occurs and when formed during the normal course of cooling the inner zones are more magnesian, the outer more calcic. To be sure we are dealing with purely lime-magnesian pyroxenes, but it might be well to recall here that, in spite of the fact that we are prone to speak of the pyroxenes as ferro-magnesian minerals, the common pyroxene of igneous rocks usually contains lime, magnesia and iron in proportions in the order named.

Reference has already been made to the enstatite-augites of Wahl and attention called to their similarity in optical properties with the artificial pyroxenes. The analogy extends to some of their other relations. For example, Wahl has shown that, in a great variety of rocks bearing these enstatite-augites, the earlier pyroxene crystals are more magnesian, the later more calcic. This is sometimes true of the earlier and later parts (zones) of the same crystal, a fact which has been pointed out above for the artificial crystals.

It would appear, then, that pyroxenes more or less similar to the artificial lime-magnesia pyroxenes (differing from them principally in their iron content) have considerable importance in igneous rocks.

It has been shown in the optical part of this paper that, for the artificial lime-magnesia pyroxenes, the composition can be determined fairly closely from the optical properties. The ability to do so for the natural pyroxenes of rocks is very desirable and the present results may be considered a step in that direction. The lime-soda feldspars are at present the only isomorphous series of rock-forming minerals in which chemical composition and optical properties can be correlated with fair accuracy. Among recent studies in this direction that of Ford on the amphiboles may be noted. Until a great deal of such work has been accomplished, the determination of the proportions of minerals in a rock, as by the Rosiwal method, can, in the usual case, have little value.

Resorbed Olivines in Natural Rocks.

It has been shown that in the artificial melts discussed, from which olivine is the first mineral to crystallize, the olivine is at a later stage either partly or completely redissolved, giving pyroxene by reaction with the liquid. This resorption takes place in the normal course of crystallization on cooling and is the necessary result of equilibrium between the phases. In natural rocks the resorption of olivine often takes place, an example occurring in the case of the Palisade diabase of New Jersey, where, in the contact facies, olivine with reaction rims of enstatite is observed.* Such resorption has sometimes been assumed to imply some such drastic change as the sudden relief of the pressure to which the magma was subjected and the consequent instability of minerals formed under the higher pressure. Minerals exhibiting resorption are, moreover, sometimes assumed to have formed from a magma having a composition different from that of the rock in which we find them and, perhaps, to have sunk into a magma which exerted a solvent action upon them. In the case of olivine such assump-

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* Lewis, J. V., Ann. Rep't, State Geologist, New Jersey, 1907, 133.

tions are unnecessary. Resorption may have occurred during simple cooling under uniform conditions, the only change of composition being that in the still fluid portion of the magma as a necessary consequence of the separation of crystals.

Recurrent Crystallization.

It has been shown in the discussion of crystallization that, in certain of the artificial mixtures, forsterite may crystallize out, become completely redissolved (resorbed) and again crystallize out at a lower temperature. This behavior, in a comparatively simple system, illustrates how complicated the so-called 'order of crystallization' may be in a system so complex as an igneous magma. In natural rocks a great number of solid solution series are known to occur and there are a great many possibilities, or better necessities, of equilibrium in the liquid between orthosilicate and metasilicate molecules as exhibited, in the artificial system and in natural rocks, by pyroxene and olivines, between feldspar and feldspathoid molecules and of other equilibria which readily suggest themselves. The theoretical discussion of crystallization in such systems in terms of simple eutectics cannot lead to any useful conclusion.

We have, then, in the artificial system studied, a concrete example of the possibility of crystallization in 'two generations.' It is not necessary, however, that the two generations of any mineral, often observed by the petrographer, should have come about in a similar manner. Perfectly continuous crystallization may give the appearance of crystallization in two generations. The earliest formed crystals may continue to grow in size up to a certain point, when the increasing viscosity or the increasing ratio of crystals to liquid may necessitate the formation of new centers of crystallization. In such a case there may be larger phenocrysts and smaller groundmass crystals of a certain mineral though crystallization was perfectly continuous.

The Significance of Zoned Crystals.

The distinction between the two types of crystallization described for the artificial, pyroxene-bearing melts should be carefully considered in any discussion of the crystallization of an igneous rock magma. In the first type of crystallization, the liquid is at equilibrium at any temperature with all the crystals, and with all parts of the crystals, existing in it. In the second type the liquid is at equilibrium at any temperature only with the crystals separating at that temperature. To realize the first type it is often necessary that crystals already separated should be redissolved and that mix-crystals already separated should change their composition, whereas in the second type no such changes take place. Between the extremes of perfect adjustment of equilibrium between the liquid and the early-formed crystals and complete lack of adjustment there is every stage of partial adjustment. If the mechanism of crystallization is considered, it is apparent that perfect adjustment must be exceedingly difficult to obtain. In order to change the composition of a mix-crystal there must be a diffusion of material in the solid crystal itself and an interchange of material between it and the liquid. In the meantime crystallization of a further quantity of mix-crystal of somewhat different composition is in progress and is almost certain to take place as a layer or zone about the early crystal as a nucleus, rather than to form a new nucleus. Unless diffusion in the solid can take place fast enough to bring about a change, the composition of this outer layer will remain different from that of the layer it surrounds, while still other layers are added. Cooling at an exceedingly slow rate might, perhaps, bring about perfect adjustment, but usually zoned crystals will result.

It is well known that zoned crystals are common in natural rocks. The significance of the formation of zoned crystals is great because, as has been shown in the discussion of crystallization of the second type, the temperature of final solidification is thereby very much lowered—the temperature and time interval of crystallization, therefore, much increased.*

Even when the cooling is extremely slow, a factor other than zoning may intervene to bring about the same result of preventing the early crystals from participating in any interchange with the liquid necessitated by equilibrium at a lower temperature. This factor is the rising or sinking of crystals under the action of gravity as they grow in the liquid.

Consequences of the Possible Sinking of Early Crystals in a Fluid Magma.

The idea that the sinking of crystals in a fluid magma has some importance in the differentiation of igneous rocks has recently been gaining ground. That such action must take place seems hardly debatable, only its relative importance is at issue.

In the melts here described, from our precise knowledge of equilibrium, we are able to determine definitely the effect of a possible settling of crystals. In discussing the crystallization

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* See also N. L. Bowen: The Melting Phenomena of the Plagioclase Feldspars, this Journal (4), xxxv, 597, 1913.

of the melts, the behavior of a mixture of composition M, fig. 17, was described. If we imagine that the olivine crystals settled towards the lower layers, then, as the temperature of the point K is approached, the composition of these layers would lie between M and A and of some of the upper layers between P and K. On further cooling the various layers would behave quite differently, those having an abundance of olivine would crystallize to a mixture of pyroxene and olivine, those with only a small amount of olivine would have the olivine completely resorbed and would finally crystallize to a mixture of pyroxene and silica (cristobalite or tridymite). Thus the settling of crystals may bring about not merely a difference in the proportions of the minerals in various layers, but may produce a partially different assemblage of minerals.

The portions which crystallized to pyroxene and silica would, moreover, become completely crystallized at a lower temperature than would the other portions and might, perhaps, show an intrusive relation to the olivine-bearing portions. Such a result would be impossible if the minerals showed the simple eutectic relation, even if there were settling of crystals, for in this case all parts would have some share of liquid until the time of simultaneous final solidification of all the layers, assuming, of course, all the layers to have the same temperature. In the case of a difference of temperature in different layers, the cooler layers would necessarily become completely solid before the warmer layers when eutectic relations prevailed, however great a quantity of crystals had settled. In the melts described, however, the settling of olivine could bring it about that a lower, olivine-rich layer might become completely solid when at a higher temperature than an upper layer, poor in olivine, and still largely liquid.

But this result may be accomplished, not by the settling of olivine alone, but also by the settling of the early-formed, more magnesian pyroxenes and the continued concentration of calcic pyroxenes in the liquid. The crystallization would then tend towards crystallization of the second type and the result would be the same as when zoned crystals are formed. Here again one portion might become completely solid even when at a higher temperature than another portion still partly liquid. A similar behavior is possible in any melt that deposits mix-crystals of which one constituent has a considerably higher melting point than the other, as is notably the case with that very important rock-forming series, the plagioclase feldspars. Thus it seems possible that a homogeneous magma, containing substances capable of forming mix-crystals, as do all magmas, could become differentiated through crystallization into parts which gave evidence of having solidified at different times and which had quite different compositions. Neither is it necessary, as it would be in the case of simple eutectic relations, that the part lying towards the cold contact should be the one giving evidence of having solidified first, for it would be possible to have the temperature of final solidification of such portions so lowered by the sinking out of crystals that they might still be largely liquid when a lower and hotter portion had already completely solidified.

To the writer it seems that the settling out from a basic magma of the more calcic plagioclases and the pyroxenes rich in magnesia and iron is the dominant control in the differentiation of the ordinary lime-alkali series of igneous rocks. Possibly causes other than gravity, which may bring about a similar relative movement of crystals and liquid, may be of equal importance, an example being the intrusion or forcing out of the liquid phase at a stage when most of the magma has crystallized. It would therefore be better to state that fractional crystallization, as opposed to fractionation in the liquid state, when aided by the processes mentioned, appears to be the prime factor[*] in the differentiation of the series mentioned.

In making this result possible the occurrence of mix-crystals is one of the fundamental factors.

Dissociation in the Liquid Phase and its Relation to Crystallization.

There is one question on which the behavior of the artificial melts throws some light and of which some mention might be made, that is the question of the state of combination of the various oxides in the liquid state. It has been maintained by some that the oxides must exist uncombined; at the time of crystallization they combine and the combinations may be different under different physical conditions. Unless this is true, it is stated, the same magma could not under different conditions give rise to different rocks. To this argument the objection has been raised that there is no evidence that the heat of combination is set free at the time of crystallization and that the oxides must therefore be combined. From the viewpoint of general chemistry, it might be stated that both views are right and both wrong. We must consider that in any melt there are certain amounts of the free oxides and of all possible combinations of these oxides.[†] The necessity of such

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[*] Cf. Harker, A.: Fractional Crystallization the Prime Factor in the Differentiation of Rock-Magmas. Communicated to 12th Int. Geol. Congress, Toronto, 1913.

[†] Cf. Harker, A.: The Natural History of Igneous Rocks, p. 165.

an assumption is illustrated in the magnesia-rich mixtures of the present investigation and especially in the simple case of the mixture of composition $MgSiO_3$. The behavior of a liquid of this composition, when cooled, illustrates the fact that, in the liquid state, the whole cannot consist simply of the compound $MgSiO_3$. All possible compounds must be considered; that which separates in the solid form will be the one which, under the conditions, happens to be the first to reach its limit of solubility.

In the case of liquid of composition $MgSiO_3$ we must consider that, among others, Mg_2SiO_4 molecules are present and that, on cooling, the liquid becomes saturated with these at 1577°, forsterite separating out. On further cooling forsterite continues to separate, the liquid always remaining at the point of saturation with respect to that substance. At 1557° the liquid becomes saturated with respect to $MgSiO_3$ and clino-enstatite begins to separate. In the liquid an equilibrium exists which can be represented by the equation

$$2MgSiO_3 \rightleftarrows Mg_2SiO_4 + SiO_2$$

and at any temperature there is a definite equilibrium constant, that is, the relative proportions of the three compounds are fixed. When, at 1557°, $MgSiO_3$ separates from the liquid it is necessary that this reaction should proceed in the direction from right to left in order to maintain these proportions. This reaction lessens, however, the concentration of Mg_2SiO_4 in the liquid and since the liquid must remain at the point of saturation with respect to forsterite, forsterite must dissolve. This cycle continues, forsterite dissolving and clino-enstatite precipitating, until the whole consists of crystalline clino-enstatite.

In all the compositions lying along the line between $MgSiO_3$ and $CaMgSi_2O_6$ as far as 75 per cent $CaMgSi_2O_6$ we have, in the separation of forsterite, this direct evidence of the same equilibrium reaction in the liquid. It should not be assumed, because forsterite does not separate from liquid $CaMgSi_2O_6$ and the mixtures close to it, that this reaction does not occur. On the contrary, it simply happens that liquid $CaMgSi_2O_6$ becomes saturated on cooling with diopside first, and for this reason the whole crystallizes to diopside. Among others, a possible equilibrium in liquid diopside could be written

$$2CaMgSi_2O_6 \rightleftarrows 2CaSiO_3 + Mg_2SiO_4 + SiO_2.$$

Crystallization of diopside simply causes the reaction to proceed from right to left and the whole becomes solid diopside, the crystalline product, by itself, giving no clue to the state of combination in the liquid.

In summing up, then, it may be stated that any igneous magma or mineral melt may best be regarded from the viewpoint of the kinetic theory: all possible combinations and dissociations are going on simultaneously. At any temperature all the reactions have a definite rate and at equilibrium there are definite relative amounts of all the constituents. On cooling such a magma the first substance to crystallize will be that one of all those present which happens to reach first its point of saturation with respect to the liquid under the prevailing conditions. Under different conditions there may crystallize first an entirely different substance. This is true of the substance which crystallizes second and so on till all is solid. For this reason the same magma might give rise to different assemblages of minerals under different conditions. The whole reduces itself to a question of relative solubilities (relative degree of saturation) considered in conjunction with equilibrium between the molecules in the liquid phase.

Freezing-Point Lowering in Silicate Mixtures.

Many attempts have been made to calculate freezing-point lowering in silicate melts and therefrom to calculate eutectic points of various pairs of minerals. Usually the law of freezing-point lowering in dilute solutions has been used. It is well known that this law cannot apply to concentrated solutions and that even the form of equation used for concentrated solutions need correction factors when there is association or dissociation in the liquid phase. The binary system, diopside-forsterite, exhibits an extreme case of variation from the simple rules. The addition of forsterite to diopside depresses the freezing-point an almost inappreciable amount—the eutectic point at the composition 12 per cent forsterite is only about 4°–5° below the melting-point of diopside. The microscope shows that there is no solid solution, so the explanation of this slight depression must be sought in a different direction. It has already been stated as probable that diopside is dissociated in the liquid state and a possible equation for this dissociation was given.

$$2CaMgSi_2O_6 \rightleftarrows 2CaSiO_3 + Mg_2SiO_4 + SiO_2.$$

If forsterite is added to a liquid containing all the above molecules, a necessary result is the driving of the reaction from right to left and, therefore, the actual concentration of diopside molecules may be changed very little. At the freezing-point of diopside the complex liquid is just saturated with diopside molecules. The addition of forsterite (Mg_2SiO_4), if it affects very little the concentration of diopside molecules, should therefore change the freezing-point very little. The very slight effect on the freezing-point actually observed may therefore be due to the existence of an equilibrium in the liquid such as that expressed in the above equation. The equation for the actual equilibrium is probably much more complicated than the above, but, if the reasoning is correct, should contain the molecule Mg_2SiO_4 as one of the reaction products. In confirmation of this view that diopside is dissociated in the liquid state is the fact that, whereas the crystals of the $CaSiO_3$–$MgSiO_3$ series show a sharp minimum on the curve of specific volumes at the composition of diopside,* the glasses of the same series (undercooled liquid) show no minimum.† The smooth curve of specific volumes of the glasses does, however, lie distinctly below the straight line joining the volumes of the end members and may be considered to indicate, therefore, the formation of some of the denser diopside molecules in the liquid, but only in equilibrium proportions.

It is probable that more or less dissociation in the liquid state is common with silicates and, when mixed, they mutually affect each other in this respect. It is, therefore, not to be expected that, in the usual case, silicate mixtures should obey any simple law of freezing-point lowering. Disagreement with the law is, however, probably more apparent than real, for, in order to apply the law, a knowledge of the molecules present is necessary, whereas there is usually a complete lack of knowledge of this point, as well as of the heat-effects accompanying any molecular changes.

GENERAL SUMMARY.

The results obtained in the investigation of the three binary systems involved are first presented. The system diopside-silica shows the simple eutectic relation, as does also the system diopside-forsterite. The system forsterite-silica shows one intermediate compound $MgSiO_3$ (clino-enstatite) unstable at its melting-point.

In the ternary system it is found that clino-enstatite and diopside form a complete series of solid solutions (monoclinic pyroxenes) and therefore have a common field. As a further consequence of this unbroken series of solid solutions there is no ternary eutectic, the lowest point of formation of liquid in the system being the binary eutectic diopside-silica.

A brief theoretical discussion of solid solution in ternary systems is given in which the significance of certain lines, termed three-phase-boundaries, is pointed out. The results of

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* Allen, White, Wright and Larsen, this Journal (4), xxvii, 27, 1909.

† Larsen, E. S., ibid. (4), xxviii, 263, 1909.

the experimental determination of the three-phase-boundaries in the system being investigated are then presented.

The course of crystallization in typical mixtures is described and the value of the three-phrase-boundaries pointed out, especially their usefulness in determining the composition of mix-crystals separating at any temperature. In considering crystallization it is shown that crystallization may proceed according to two different methods; first, that in which the liquid is, at any temperature, in equilibrium with all the crystals and all parts of the crystals occurring in it; and second, that in which the liquid is in equilibrium at any temperature only with the crystals separating at that temperature. In a general way, crystallization of the second type is favored by quick cooling.

The importance of distinguishing between the two types of crystallization is great in the present system. It is shown that the difference between the conclusions arrived at in the present work and those arrived at in an earlier investigation of the pyroxene series carried out at this laboratory is due largely to the fact that in the earlier work crystallization of the second type occurred in many of the mixtures, whereas, if equilibrium is to be studied, crystallization of the first type must be obtained.

In the optical part of the paper the optical properties of the various crystalline phases are given. The properties of the series of monoclinic pyroxenes extending from diopside to enstatite vary continuously with composition. The artificial pyroxenes are compared with the enstatite-augites of Wahl.

In considering the bearing of the results on petrologic problems attention is called to the resorption of the olivine, forsterite, in the artificial mixtures and its probable relation to resorption of olivines in natural rocks. The consequences of the possible settling of crystals in a fluid magma (crystallization-differentiation) is discussed in the light of the facts known concerning the artificial mixtures.

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