THE SYSTEM, $MgO-FeO-SiO_2$.

N. L. BOWEN AND J. F. SCHAIRER.

INTRODUCTION.

In view of the great importance of ferromagnesian silicates as rock-forming minerals a study of equilibrium in the system, $MgO-FeO-SiO_2$, may be expected to reveal facts and relations of much value in deducing the conditions of formation of many rocks. With these considerations in mind investigation of the system was undertaken. The procedure adopted and the results attained are here presented.

FUNDAMENTAL SYSTEMS.

Of the three fundamental systems two had already been made the subject of detailed studies. These are the system, $MgO-SiO_2$,[1] and the system, $FeO-SiO_2$.[2] The equilibrium diagrams are here reproduced in Figs. 1 and 2, respectively. The third fundamental system, MgO-FeO, has not been investigated in detail. It has, in itself, no great petrologic importance. The one end member, FeO, melts incongruently with separation of metallic iron and formation of a liquid containing oxygen in excess of the ferrous ratio, and this fact so complicates the detailed relations, that for their full elucidation a greater amount of investigation would be required than is warranted for our present purposes. Nevertheless, the broader relations are sufficiently clear. We have ascertained that MgO and FeO form a complete series of solid solutions, which we here term magnesio-wüstites. We find also that the temperature of melting rises rapidly as MgO is added to FeO, soon reaching a value above the melting point of iron and thus precluding further investigation by the method here followed. If the incongruent character of melting, with consequent complications, is neglected, the form of equilibrium diagram indicated by these facts is given in Fig. 3.

---

[1] Bowen, N. L., and Andersen, Olaf: This Journal, **37**, 487-500, 1914. Greig, J. W.: This Journal, **13**, 15, 1927.

[2] Bowen, N. L., and Schairer, J. F.: This Journal, **24**, 177-213, 1932.

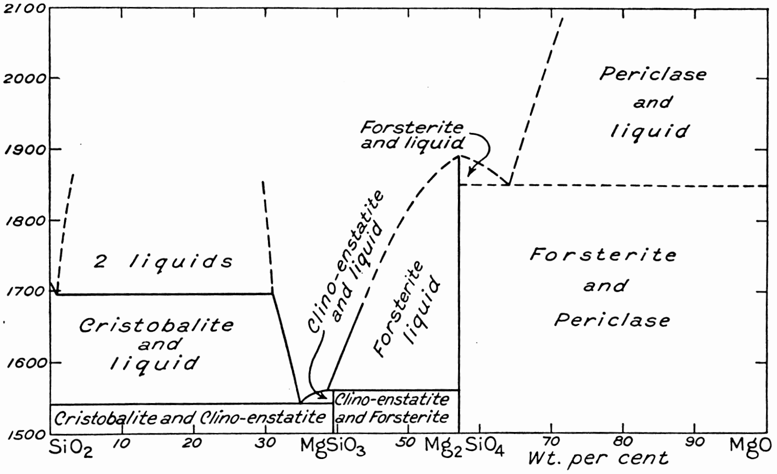

Fig. 1. Equilibrium diagram of the system, MgO-SiO_2.

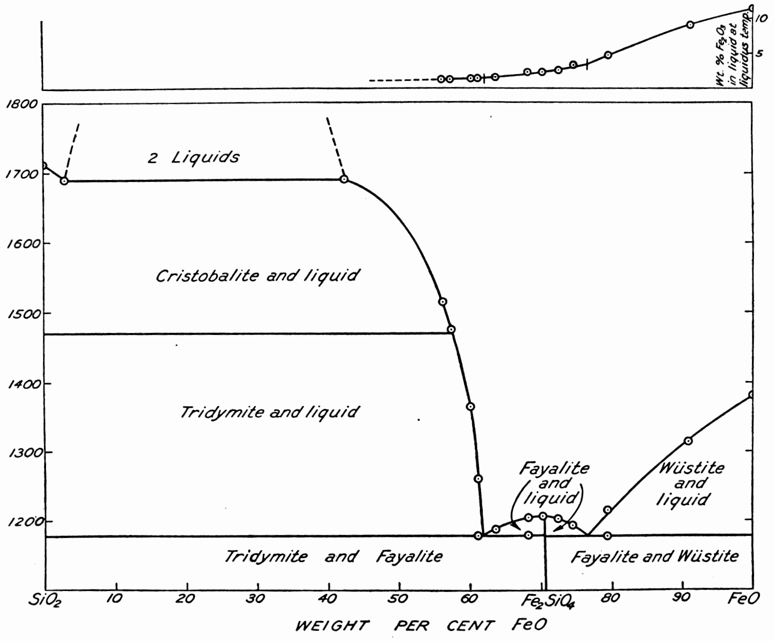

Fig. 2. Equilibrium diagram of the system, FeO-SiO_2.

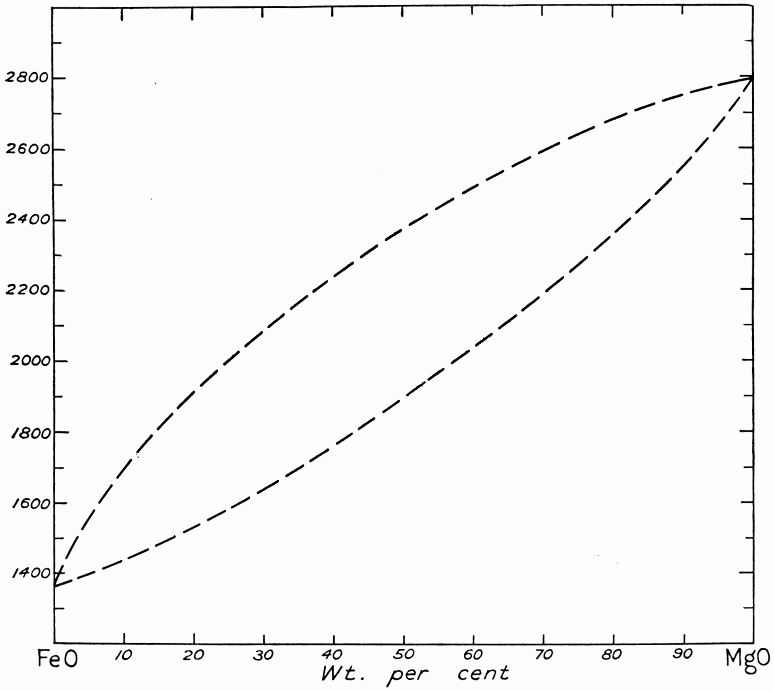

Fig. 3. General form of equilibrium diagram of the system, MgO-FeO.

METHOD OF INVESTIGATION.

Preparation of Mixtures and Thermal Study.

The methods used for the investigation of mixtures containing iron in the ferrous state have been described in detail in the paper on the system, FeO-SiO_2, already referred to.[3] Briefly, it may be said that mixtures were prepared by taking silica, ferrous oxalate (or Fe_2O_3) and MgO in the proportions calculated to give the desired product, and melting them together three times in a platinum crucible in a Meker furnace. Thus was obtained a product deviating somewhat from the desired product by reason of a small deficiency of iron (removed by the Pt crucible) and also the existence of a little of the iron in the ferric state. Small samples of the mixture were then

---

[3] Bowen, N. L., and Schairer, J. F.: This Journal, 24, 178-186, 1932.

heated in iron crucibles in a stream of nitrogen and the temperatures of beginning of melting, of completion of melting, and of any other changes of phase were determined by the method of quenching, combined with microscopic determination of the phases in the quenched product. Upon heating in the iron crucible, a small change of composition of the charge occurs which is principally due to reduction of ferric oxide by the iron crucible and consequent increase of the total iron content of the charge. This increase may partly balance, or it may more than balance, the deficiency produced by melting in platinum. In all cases it was, therefore, necessary to make a chemical analysis of each mixture after a run in an iron crucible at the temperature at which a change of phase was found to occur. Ordinarily, the temperature of the run made for this purpose was that at which completion of melting took place and the analysis thus gave the composition of the liquid at the liquidus point for the particular mixture. By repeating this procedure for a series of mixtures and plotting the determined liquidus temperatures and analyzed compositions (with microscopic determination of the crystal phases) the liquidus surfaces can be constructed. In a similar manner the solidus relations may be determined.

The readings of the thermocouples used to measure temperatures were checked by frequent calibration at standard melting points defined as follows: NaCl 800.4, Au 1062.6, Li_2SiO_3 1201, $CaMgSi_2O_6$ 1391.5, and Pd 1549.5.

Methods of Chemical Analysis.

The methods used in determining ferrous and ferric oxides have been described in detail in a former paper.[4] The relative proportions of MgO and SiO_2 are, of course, fixed by synthesis and require no analytical determination.

EXPERIMENTAL RESULTS.

The results of the determination of the temperatures of the phase changes by the method of quenching, together with the analyses of the mixtures, are given in Table I. It will be noted that, even after holding the mixtures in a molten state in an iron crucible in nitrogen, some of the iron remains in the

---

[4] Bowen, N. L., Schairer, J. F., and Posnjak, E.: This Journal, **26**, 197, 1933.

TABLE I.

(a) Mixtures Closely Approximating the Metasilicate Join.

Composition of liquid at liquidus temperature				Temp. of completion of melting ± 4°	Primary phase	Temp. of beginning of melting ± 8°	Refractive index of glass	Composition reduced to	
FeO	Fe_2O_3	MgO	SiO_2					$MgSiO_3$	$FeSiO_3$
17.53	0.26	27.63	54.58	1495	clino-pyroxene	1415	1.616	..*	..*
21.15	0.28	24.21	54.36	1465	clino-pyroxene	1375	1.621	60	40
27.84	0.66	19.72	51.78	1427	clino-pyroxene	1340	....	..*	..*
30.10	0.45	17.86	51.59	1416	clino-pyroxene	....	....	45	55
32.38	0.48	16.03	51.11	1400	tridymite and clino-pyroxene	1305	1.648	40	60
38.43	0.59	11.88	49.10	1420	tridymite	....	....	..*	..*
44.22	0.89	7.81	47.08	1460	tridymite	....	....	..*	..*
49.23	1.22	3.89	45.66	1500	cristobalite	....	....	..*	..*

* These mixtures deviate slightly from metasilicate compositions. They nevertheless serve to fix the position of isotherms at points very close to the metasilicate join.

TABLE I—*Continued.*

(b) Mixtures Closely Approximating the Orthosilicate Join. Primary Phase Olivine.

Liquidus Determinations

Composition of liquid at liquidus temperature				Temperature of completion of melting	Composition reduced to	
FeO	Fe_2O_3	MgO	SiO_2	± 4°	Mg_2SiO_4	Fe_2SiO_4
61.89	1.65	5.72	30.74	1340	10	90
56.10	1.46	11.08	31.36	1450	20	80
50.66	1.58	14.53	33.23	1495	25	75

Solidus Determinations

Approximate bulk composition of mixture		Temperature	Composition of solid phase determined optically	
Mg_2SiO_4	Fe_2SiO_4	± 4°	Mg_2SiO_4	Fe_2SiO_4
10	90	1275	20	80
10	90	1317	30	70
25	75	1410	46	54
25	75	1440	52.5	47.5
25	75	1465	55	45
40	60	1495	59	41

TABLE I—*Continued.*

(c) Mixtures Having Olivine as the Primary Phase. See also Table I(b).

Composition				Temperature of completion of melting ± 4°	Refractive index of glass ± .003
FeO	Fe_2O_3	MgO	SiO_2		
58.64	1.77	4.95	34.64	1305	....
57.73	1.38	3.07	37.82	1242	1.750
54.16	1.25	4.95	39.64	1268	....
52.59	0.95	5.66	41.80	1275	1.725
50.25	1.13	9.72	38.90	1345	1.730
53.66	1.06	8.05	37.23	1335	....
49.33	1.16	12.88	36.63	1430	....
46.18	0.93	9.40	43.29	1315	1.702
44.80	1.11	10.80	43.29	1350	1.700
44.72	0.76	8.92	45.60	1305	....
39.05	1.04	14.98	44.93	1400	1.687
44.30	1.25	14.85	39.60	1435	1.716
43.01	1.07	18.30	37.62	1509	....
39.88	0.77	19.78	39.57	1509	....
34.90	0.79	19.78	44.53	1470	....
37.30	0.61	14.55	47.54	1380	1.668
30.66	0.79	21.55	47.00	1470	1.661
26.47	0.58	22.40	51.55	1463	....
26.51	0.58	24.30	48.61	1485	1.648
19.02	0.35	26.88	53.75	1485	....

TABLE I—*Concluded.*

(d) Mixtures Having Clino-pyroxene as Primary Phase. See also Table I(a).

Composition				Temperature of completion of melting ± 4°	Refractive index of glass ± .003
FeO	Fe_2O_3	MgO	SiO_2		
19.21	0.51	24.80	55.48	1475	....
26.44	0.59	19.45	53.52	1430	1.633
28.35	0.69	19.30	51.66	1424	1.642
40.05	0.63	11.87	47.45	1352	1.672
(e) Mixtures Having Tridymite as Primary Phase. See also Table I(a).					
51.36	0.89	4.78	42.97	1370	1.713
(f) Mixtures Having Cristobalite as Primary Phase. See also Table I(a).					
15.61	0.37	25.70	58.32	1495	....
29.83	0.59	15.91	53.67	1505	1.638

ferric state. In the former papers it was shown that even after melting in an iron crucible in an evacuated, sealed, silica-glass tube, there is still persistence of some ferric iron in the silicate liquids, and reasons were there given for the belief that the small amount of ferric iron persisting in the nitrogen runs represents equilibrium with metallic iron. The same condition must be regarded as obtaining in the present mixtures as well. Iron is incapable of further reducing the Fe_2O_3 content of these silicate melts. An attempt at reduction with the aid of a reducing agent would result only in the separation of metallic iron from the liquid without decrease of its Fe_2O_3 content.

The manner in which the equilibrium content of Fe_2O_3 varies with the composition of the liquid is shown in Fig. 4. The amount of Fe_2O_3 is not proportional to the total iron but it is much more nearly so than in the system, CaO-FeO-SiO_2.[5]

There is always some iron in the ferric state in the liquid which is in equilibrium with the various crystalline ferrous silicates of the system and with iron. It follows that these silicates must melt incongruently with separation of iron. This behavior has been demonstrated for the compound fayalite in the former papers.

For a full and accurate presentation of the experimental

---

[5] Cf. this Journal, **26**, p. 203, Fig. 4, 1933.

results it would, in the light of the above facts, be necessary to refer them to quaternary equilibrium in the system, MgO-Fe-Fe_2O_3-SiO_2. This would require the use of a tetrahedron for the graphic presentation. The results are much more conveniently and lucidly presented by neglecting the small amounts of Fe_2O_3 in the liquid, calculating the total iron as FeO and plotting the data on a ternary diagram. In the following this course has been adopted, but we must emphasize that the liquids always contain a little ferric iron, the approximate amount of which can be ascertained for any liquid by reference to Fig. 4. It is not possible for us to remind the reader repeatedly of this fact. Throughout the paper, whenever we speak of a binary or a ternary system (or a binary or ternary invariant point) it is to be borne in mind that the system (or point) can be treated as binary or ternary respectively only when the small content of Fe_2O_3 is arbitrarily regarded as FeO.

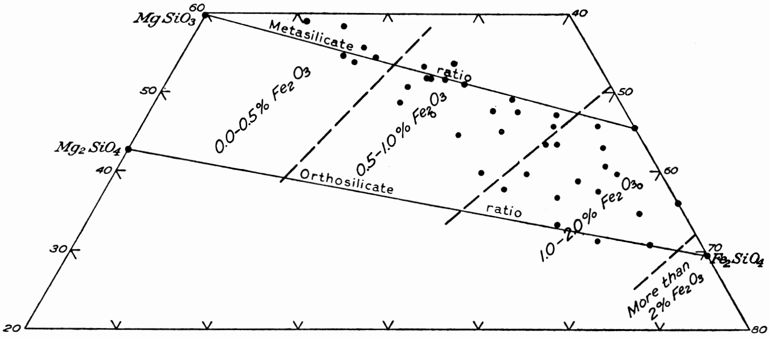

Fig. 4. Diagram showing the approximate Fe_2O_3 content of liquid mixtures of MgO, SiO_2 and Fe oxide, in equilibrium with metallic iron. The position of the figure in the general triangle is readily made out by comparison with Fig. 5.

EQUILIBRIUM DIAGRAMS.

In Fig. 5, based on the results given in Table I, are shown the fields in which each of the solid phases encountered in the system occurs as the primary phase in equilibrium with liquid. Fig. 6 gives the same information together with isotherms showing the temperature of complete melting (solution) of the primary phase for the various compositions, in other words, the temperatures of points on the liquidus surfaces. Although Figs. 5 and 6 are largely self-explanatory, a few comments may be in place.

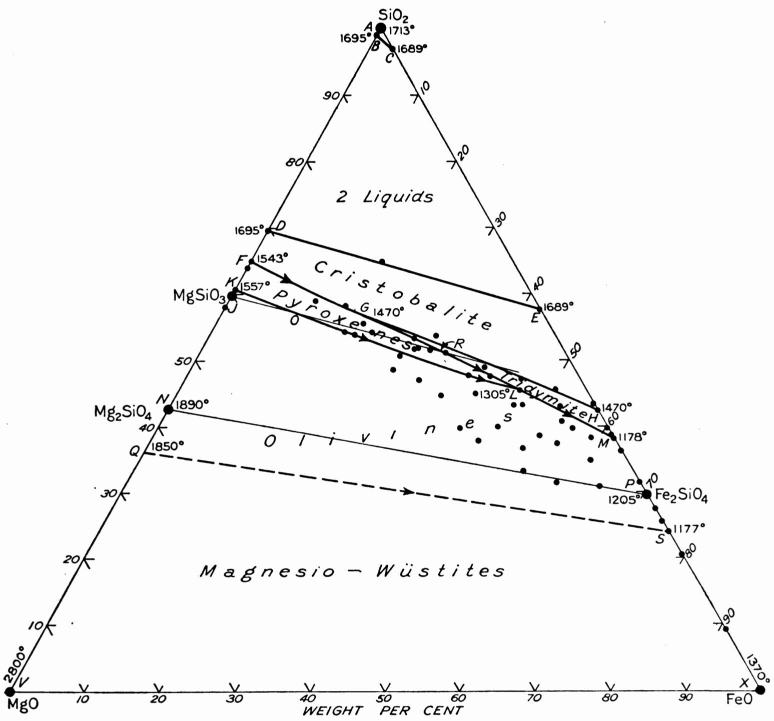

Fig. 5. Equilibrium diagram of the system, MgO-FeO-SiO$_2$, showing the fields of stability of crystalline phases in contact with liquid. (Small amount of Fe$_2$O$_3$ in all liquids; see Fig. 4 and Table I).

The Various Fields and Their Boundary Curves.

The field of any crystalline phase in Fig. 5 is, of course, the projection of its liquidus surface upon the triangular base of the solid T-X (temperature-composition) model. The field of cristobalite is, therefore, in two parts, *ABC* and *DFGHE*, corresponding with the division of the cristobalite liquidus surface into two parts separated by an area in which no liquidus surface exists.[6] This is the area *BCED* (marked

---

[6] The liquidus surface of any crystalline phase may be defined as that T-X surface which is the locus of all points each of which represents simultaneously the composition of a liquid and the temperature at which that liquid is in equilibrium with said crystalline phase. Since no liquid of composition represented by a point within the area *BCED* can exist at temperatures where cristobalite (or any other crystalline phase) can co-exist with it, the area *BCED* is properly regarded as an area in which there is no liquidus surface.

two liquids) the boundaries of which have been determined by Greig and the curves *BC* and *DE* are taken from his work.[7] Our investigation was confined to temperatures below 1520° on account of the limitation imposed by the melting point of our iron crucibles.

By reason of the ready mutual replacement of Mg and Fe″ in their silicate compounds and the failure of double salts, the number of fields and field boundaries in the system is reduced to a minimum. For the same reason there is no ternary eutectic in the system; the low points lie on the FeO-SiO_2 side of the triangle and all fusion surfaces slope towards that side. This makes for great simplicity of the fusion surfaces. The one notable complication of the liquidus relations is the fact that the field of the metasilicates or monoclinic pyroxenes *FLK*

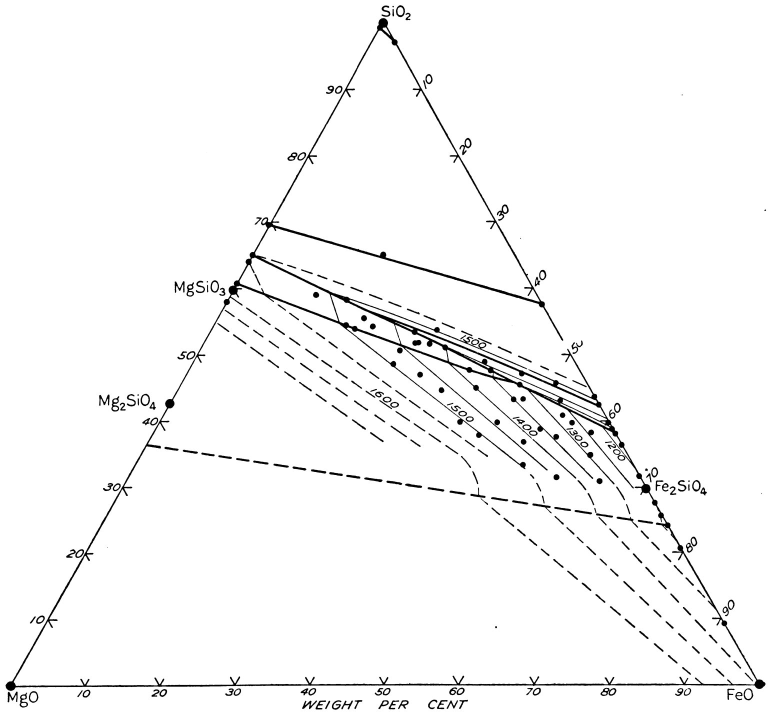

Fig. 6. Same as Fig. 5 with isotherms added.

---

[7] Greig, J. W.: This Journal, 13, 144, 1927.

(Fig. 5) is wedge-shaped and vanishes to a point at *L*. Beyond this point no metasilicate field is interposed between the orthosilicate (olivine) field and the silica (tridymite) field. Some such relation was, of course, to be expected since the compound $FeSiO_3$ does not exist, although solid solutions containing nearly 90 per cent of that molecule can form. It is of interest that of these metasilicate solid solutions (pyroxenes) the more magnesian (*J* to *O*) lie in the olivine field. Those of intermediate composition (*O* to *R*) lie in the pyroxene field whereas those rich in iron (from *R* onward) lie in the field of silica in one form or another. The one end of the series thus melts incongruently with separation of olivine, a less siliceous phase, whereas the other end of the series melts incongruently in what we may term the opposite direction, that is, with the separation of a more siliceous phase, indeed silica itself. This change of character of the incongruent melting in a single solid solution series has not been observed in any system nor has it been discussed theoretically. The details of the relations involved will be brought out later with the aid of a diagram representing a section along the metasilicate join.

The boundary curve *QS* between the fields of olivine and of magnesio-wüstite is only roughly located except at *S* and is therefore shown as a broken line. Of the olivines the complete series *N*-*P* lies in the olivine field.

Invariant Points.

The invariant points are listed in Table II. The only ternary invariant point on the liquidus surface, other than the inversion point *G*, is the point *L* at which tridymite, monoclinic pyroxene, and olivine are in equilibrium with liquid of composition *L* at 1305°. The exact composition of the several phases is given in Table II. As already indicated, the point *L* is not eutectic, the reaction being liquid + pyroxene $\leftrightarrows$ olivine + silica.

The Binary System, Mg_2SiO_4-Fe_2SiO_4.

There is only one join in the ternary system that constitutes a binary system. This is the orthosilicate join, the crystalline end members being the familiar rock-forming minerals forsterite and fayalite. The relations in this system are very simple. A complete series of solid solutions of type I (Roozeboom) is formed. The equilibrium diagram is given in Fig. 7.

TABLE II.

Invariant Points.

Letter (Fig. 5)	Temp. ° C	Phases
		Unary
A	1713 ± 5	Cristobalite and liquid SiO_2 (Greig)
N	1890 ± 20	Forsterite and liquid Mg_2SiO_4
P	1205 ± 3	Fayalite and liquid Fe_2SiO_4
V	2800	Periclase and liquid MgO (Kanolt)
		Binary
B	1695 ± 5	Cristobalite, liquid B (MgO 0.8 SiO_2 99.2) and liquid D (MgO 31 SiO_2 69) (Greig)
D	1695 ± 5	same as B (Greig)
C	1689 ± 15	Cristobalite, liquid C (FeO 3 SiO_2 97) and liquid E (FeO 42 SiO_2 58) (Greig)
E	1689 ± 15	same as C (Greig)
F	1543 ± 2	Cristobalite, clino-enstatite and liquid F (MgO 35 SiO_2 65)
K	1557 ± 2	Forsterite, clino-enstatite and liquid K (MgO 39 SiO_2 61)
H	1470 ± 10	Cristobalite, tridymite and liquid H (FeO 57.5 SiO_2 42.5)
M	1178 ± 2	Tridymite, fayalite and liquid M (FeO 62 SiO_2 38)
Q	1850 ± 20	Forsterite, periclase and liquid Q (MgO 64 SiO_2 36)
S	1177 ± 5	Fayalite, wüstite and liquid S (FeO 76 SiO_2 24)
		Ternary
G	1470 ± 10	Cristobalite, tridymite, clino-pyroxene ($MgSiO_3$ 86 $FeSiO_3$ 14) and liquid G (MgO 23.5 FeO 20 SiO_2 56.5)
L	1305 ± 5	Tridymite, clino-pyroxene ($MgSiO_3$ 38 $FeSiO_3$ 62), olivine (Mg_2SiO_4 32 Fe_2SiO_4 68) and liquid L (MgO 9 FeO 46 SiO_2 45)

The curves are determined only up to 1500°, below which temperature they are shown as full lines. Above this temperature they are produced to meet at the melting point of forsterite, 1890°, and are shown as broken lines. The liquidus is determined by the usual method of finding the temperature of final disappearance of crystals and is very accurately placed. The materials do not lend themselves to determining the solidus by finding the temperature of beginning of melting because it is impossible to get them in a perfectly homogeneous condition, i.e., free from zoning. The solidus was therefore determined by holding a mixture at a measured temperature at which it consisted of liquid and crystals, and then quenching. The product of such procedure consists of homogeneous, euhedral crystals of olivine (the primary phase) embedded in a feathery aggregate of olivine formed by rapid crystallization. By determining the optical properties of the euhedral crystals the composition of the solid phase and therefore the position of the solidus for the temperature of the run was fixed. The accuracy is not as great as that attained in the fixing of points on the liquidus. The error may probably be as much as 3 to 4 in the percentage of forsterite and fayalite in the crystals.

The determinations upon which the position of solidus and liquidus is based are given in Table I.

A diagram of the type thus determined for the olivines is so familiar to petrologists in the plagioclase diagram that no special discussion of it need be given.

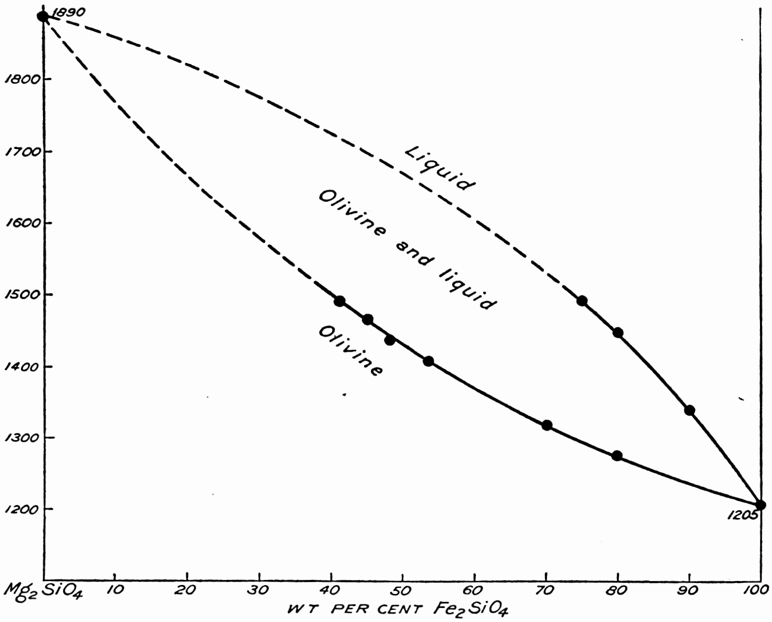

Fig. 7. Equilibrium diagram of the system, Mg_2SiO_4-Fe_2SiO_4.

The Metasilicate Join.

Although the metasilicate join does not represent a binary system, nevertheless many of the relations of metasilicate compositions are best brought out with the aid of a section along this join. The resultant diagram is given in Fig. 8, where the curves that refer to binary equilibrium are shown in heavy lines, and those referring to ternary equilibrium in lighter lines. These lighter lines, therefore, give only the temperature at which phase changes occur in a mixture of a given total composition. They do not give the composition of all the phases concerned in the equilibrium, since these relations can be shown only with the aid of a ternary diagram. It will be noted that only the curves *BS* and *OR* with *BO* and *SR* and the curves *KY* and *KX* indicate binary equilibrium. All other relations depicted are ternary.

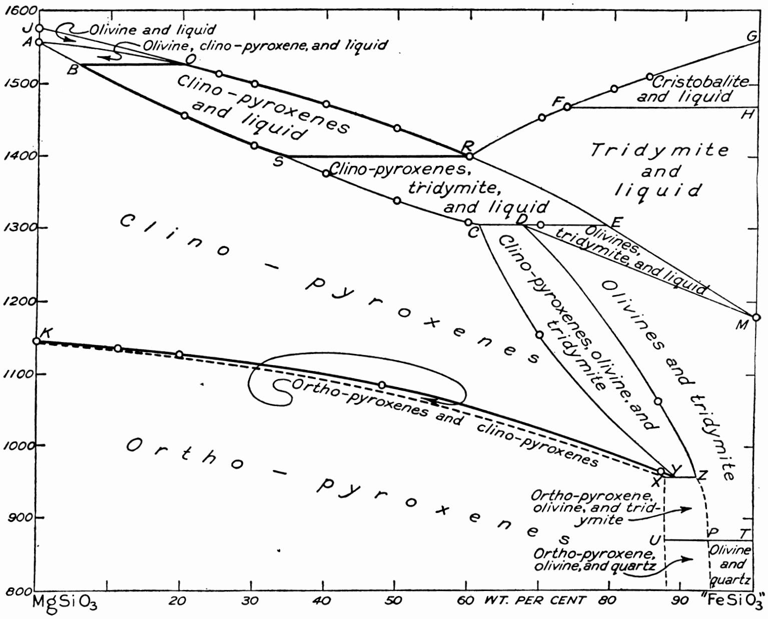

Fig. 8. Equilibrium diagram of mixtures of metasilicate ratio. Heavy curves refer to binary equilibrium and light curves to ternary equilibrium. (Binary and ternary respectively only when small amounts of Fe_2O_3 present in liquids are treated as FeO, see Fig. 4.)

The Relation between Orthorhombic and Monoclinic Metasilicates of Fe″ and Mg.

At low temperatures all metasilicate mixtures containing up to nearly 90 per cent $FeSiO_3$ exist, at equilibrium, as orthorhombic pyroxenes, corresponding with the natural enstatite-hypersthene series. At higher temperatures the same mixtures exist, at equilibrium, as monoclinic pyroxenes, corresponding with the less well known clino-enstatite, clino-hypersthene series. Members of the two series bear an enantiotropic relation to each other. The inversion temperature, which is at 1140° at the $MgSiO_3$ end of the series, falls off with increase of $FeSiO_3$ as shown by the curve KY, and at the extreme iron-rich member it lies at 955° approximately.

This conclusion is somewhat at variance with that reached by earlier investigators, but appears to be the only one justified by the facts now available. In the earlier work, which was confined to the magnesian end-member, it was found that enstatite could be transformed at high temperatures to clino-enstatite but the reverse change was not accomplished, and for that reason the inversion was regarded as irreversible and enstatite as a monotropic form.[8]

In the present study we used natural pyroxenes in part and also synthetic materials. We have found it impossible to induce any synthetic metasilicate mixture of the system to crystallize completely in the orthorhombic form. When glass is devitrified at low temperatures a fibrous product is obtained which, in the case of the magnesian member, was regarded as orthorhombic by the earlier investigators. Though this conclusion seemed then to be justified, examination by X-rays of material so prepared, including some made by the earlier investigators, shows that the powder pattern does not correspond with that of enstatite.[9] Such preparations cannot, therefore, serve as a starting point for a study of the transformation from orthorhombic to monoclinic pyroxene, even although it is true that by heating this fibrous aggregate to a sufficiently high temperature a product definitely recognizable as monoclinic pyroxene is obtained. The supposed inversion is presumably due simply to grain growth and destruction of the fibrous character.

In order to study satisfactorily the change from orthorhombic to monoclinic it was necessary to begin with material that was unquestionably orthorhombic and the natural minerals were the only substances meeting that requirement. The natural pyroxenes used were enstatite from the Bishopville meteorite, enstatite from Espedalen, Norway, bronzite from

---

[8] Allen, Wright, and Clement: This Journal, 22, 385-438, 1906.

[9] This comparison was kindly made for us by Dr. E. Posnjak.

Bonin Islands, bronzite from bronzitite, Jagdlust, South Africa, hypersthene from Mt. Dore, Auvergne, and iron hypersthene from Tunaberg, Sweden. Chemical analyses of these pyroxenes are give in Table III. Natural pyroxenes have the disadvantage that they always contain some constituents other than the components of the system now under investigation, but the enstatites and bronzites used show only moderate amounts of these extraneous oxides. The hypersthenes are not so satisfactory in this respect, especially in their high content of MnO, but the results obtained with them bear such a relation to those obtained with the purer members as to suggest that the impurities do not exert a pronounced effect upon the inversion temperature. For all the iron-bearing materials

TABLE III.

Chemical Composition of Orthorhombic Pyroxenes.

	I	II	III	IV	V	VI
SiO_2	59.97	57.28	55.04	55.40	[48.2]	47.46
TiO_2	...	0.05	...	0.10	...	0.03
Al_2O_3	...	0.90	0.88	1.60	...	0.14
Cr_2O_3	...	...	0.49	0.65	...	...
Fe_2O_3	0.40	0.42	...	nil	...	0.34
FeO	...	6.43	9.40	9.35	28.4	42.23
MnO	...	tr.	0.18	0.15	5.2	3.88
NiO	...	...	...	0.10	...	...
CaO	...	0.13	1.55	0.45	1.5	1.05
MgO	39.34	34.94	32.65	32.45	16.7	5.05
Na_2O	0.74	0.22	...	tr.	...	...
K_2O	tr.	0.01	...	tr.	...	...
H_2O+	...	0.13	0.45	nil	...	0.07
H_2O-	...	...	...	0.15	...	...
P_2O_5	...	...	...	0.20	...	...
CO_2	...	...	...	tr.	...	...
	100.45	100.51	100.64	100.60	[100.0]	100.25

I Enstatite, Bishopville meteorite.
Smith, J. Lawrence, This Journal, 36, 225, 1864.
II Enstatite, Espedalen, Norway.
Washington, H. S., and Merwin, H. E., Am. Min., 8, 64, 1923.
III Bronzite, Bonin Islands.
Kikuchi, Y., Jour. Coll. Sci. Imp. Univ. Japan, 3, 67, 1889.
IV Bronzitite, Jagdlust, Oliphants River, South Africa.
Hall, A. L., Geol. Survey, Union S. Africa Mem. 28, 315, 1932.
V Hypersthene, Mt. Dore, Auvergne, France.
Des Cloizeaux, Min. II, xviii, 1874.
VI Iron-hypersthene, Tunaberg, Sweden.
Sundius, N., Sveriges Geol. Undersök. Årsbok 26, No. 2, p. 6, 1932.

it was necessary to conduct the heating in a sealed, evacuated silica-glass tube in order to avoid oxidation of ferrous iron.

It is especially noteworthy that, while the members approaching the two ends of the series are transformed readily into the monoclinic form, intermediate members experienced definite transformation only with the aid of a "catalyst." Thus the two bronzites can be heated for hours at temperatures more than 300° above their true inversion temperature, even at temperatures where they are partly melted, without visible transformation. That this behavior is due merely to sluggishness of transformation is shown by the fact that, if a very small quantity of NaF is added to these bronzites in the sealed silica tube, the inversion takes place readily at the temperature where it is to be expected from the behavior of other members of the series. We have obtained no light on the manner in which the fluoride accomplishes this result.

Some details of the results may now be pointed out. When enstatite of the Bishopville meteorite is heated at 1150° for 4 hours partial transformation is readily made out. It manifests itself under the microscope as twinned lamellae of the monoclinic form on the edges and corners of the powdered grains. At times small grains are transformed through and through to the twinned form. The twinning is comparatively coarse and the extinction angle against the twinning some 22°. The earlier thermal studies of the relation between clino-enstatite and enstatite led to the conclusion that they were distinct crystalline forms.[10] Some opposition was raised by advocates of the concept of polysymmetry who contended that enstatite was merely clino-enstatite sub-microscopically twinned.[11] The appearance of twinning upon heating would, under this concept, be due to a growth of the twin lamellae from sub-microscopic dimensions. There would naturally be a stage during this growth at which the lamellae would be barely distinguishable under the microscope. Such a stage is never observed. The lamellae are either comparatively coarse or entirely absent and when a grain is partially transformed the boundary between the portion showing coarse lamellae and that showing none is a sharp line. These observations are altogether inconsistent with the concept of polysymmetry, but are in complete agreement with the earlier thermal studies in

---

[10] Allen, E. T., Wright, F. E., and Clement, J. K.: This Journal, **22,** 391-397, 1906. Wright, F. E.: Z. Krist., **46,** 599-600, 1909.

[11] Zambonini, F.: Z. Krist., **46,** 8, 1908.

indicating that enstatite and clino-enstatite are distinct crystalline forms of $MgSiO_3$.

When enstatite is heated for as much as 125 hours at a temperature of 1140° (only 10° lower than that at which considerable transformation takes place in only 4 hours) not a trace of monoclinic form is to be found. Such behavior is difficult to reconcile with the monotropic character of enstatite formerly suggested. A monotropic form is always unstable and a 10 degree change of temperature could hardly make such a difference in the rate of change to the stable form. The indications are rather that enstatite is stable up to about 1145° and will persist indefinitely at any temperature below that. On the other hand it will change at a measurable rate at a temperature even a few degrees above 1145°. That enstatite and clino-enstatite are enantiotropic forms with an inversion point at 1145° is the most probable interpretation. We shall find that it is supported by other observations.

The enstatite from Espedalen behaves in a quite similar manner, with the exception that some transformation can be induced at a slightly lower temperature.

Passing over the intermediate members for the moment, and turning to a consideration of the iron-rich members we find the transformation from orthorhombic to monoclinic taking place much more readily. When the temperature of iron-hypersthene from Tunaberg is raised above 960° for as little as ½ hour, complete transformation to the twinned monoclinic form takes place, whereas at 950° no change is observed in 40 hours, from which one can conclude only that there is a definite temperature of inversion at 955° approximately. For the interesting pyroxene upon which the experiments were made we are greatly indebted to Dr. N. Sundius.

In a similar manner a definite point of inversion was fixed for the hypersthene of Mt. Dore. The mineral occurs as small crystals in the vesicles of a lava for a specimen of which we are indebted to Professor Palache. Evidently the crystals of hypersthene occurring in specimens from the locality are not always of the one composition. Warren and Modell have made an X-ray study of the structure of crystals from similar rock specimens also obtained from Professor Palache. They determined the composition by measuring the optical properties, which indicated about 30 per cent $FeSiO_3$.[12] We, likewise, had such a small amount of material as to necessitate optical

---

[12] Warren, B. E., and Modell, D. I.: Z. Krist., **75**, 1-14, 1930.

determination of the composition, but we found much higher refractive indices than did Warren and Modell. Our values, $\gamma = 1.720 — 1.723$ $\alpha = 1.704 — 1.707$, indicate some 47-50 per cent $FeSiO_3$ and suggest that the crystals more nearly correspond with the material from that locality whose analysis is given in standard texts. This analysis has been given in Table III as a general indication of the composition, though their optical properties show that the actual crystals used were somewhat more magnesian. Attention is directed to the rather high content of MnO.

These crystals are transformed with great readiness to a twinned monoclinic form at any temperature above 1090° but remain unchanged at any lower temperature.

A few remarks should be made as to the orientation of the newly formed monoclinic pyroxene. From the close relationship that Warren and Modell found between orthorhombic and monoclinic pyroxenes in structure one might expect that, upon transformation, the atoms would "click" over into the new position, retaining some prominent direction common to the two structures. This expectation is not usually realized, though in the more magnesian members there is a tendency toward retention of the prism zone. In general, a single crystal or crystal fragment of orthorhombic pyroxene is transformed into an aggregate of several grains of monoclinic pyroxene of random orientation with respect to each other and to the original orthorhombic substance.

To complete the series we shall describe the behavior of the two bronzites investigated. These have nearly the same composition, as shown by the analyses in Table III, and their refractive indices are not measurably different as determined in liquids under the microscope. They have been chosen as representative of two different classes of bronzite. That from Bonin is typical of bronzite as it occurs as phenocrysts in lavas. It is free from twinning. The South African mineral is typical of the bronzites of pyroxenites and related rocks. These usually show a rather obscure lamellar twinning with extinctions up to about 9° against the composition plane. By reason of this inclined extinction they have been regarded as monoclinic by some observers and have been definitely referred to as clino-bronzites.[13] A mere inclined extinction as measured against twinning is not sufficient to disprove orthorhombic sym-

---

[13] Wagner, Percy A.: South African Journal of Industries, Industries Bulletin Series, Bull. No. 102, p. 17, 1925.

metry. Twinning on the dome 014 gives such an effect, but in some examples the twinning does not appear to follow that law.[14] However this may be, we wish to point out that these are not clino-bronzites in the strict sense of the term as here employed. True clino-bronzite shows very conspicuous twinning after 100 and the extinction angle is 33° when the composition is that of the two bronzites here investigated.

These two bronzites are identical in thermal behavior. They agree in showing extreme reluctance to transformation into the monoclinic form. They fail to invert when heated even to temperatures 300 degrees higher than that at which inversion was to be expected from the behavior of enstatites and hypersthenes and this failure was at first very puzzling. However, when a small quantity of NaF was added to the powdered mineral in the sealed tube, transformation took place readily. In working with added NaF it was found that some monoclinic crystals would form from orthorhombic even at low temperatures where we had every reason to believe that the orthorhombic was the stable form. The formation at low temperatures of a phase stable only at higher temperatures has often been observed, yet even with this complication the stability relations can be made out. In the present instance, for example, NaF causes recrystallization of bronzite to clino-bronzite, and to that form only, at temperatures above 1120°, but below 1120° newly formed crystals of bronzite appear together with the clino-bronzite, which proves the stability of the orthorhombic bronzite at temperatures below 1120° and places the transformation temperature at 1120°.

These several determinations fix the curve *KY* of Fig. 8. Theoretically there should be an inversion interval for all these solid solutions and the first small portion of the newly formed phase should be of different composition from the original material. Actually the interval of temperature (and composition) may be vanishingly small, and the indications are that it is so for the present series. No interval was found during which two phases of different composition persisted and no intimate intergrowth of two phases, such as should be formed in an inversion interval, was made out. On the contrary any grain or portion of a grain which inverted was always transformed completely to a new phase of the same composition as

---

[14] It is to be noted that the iron hypersthene of Tunaberg also shows an obscure twinning in certain sections, with extinctions from 4°-12°. Sundius, N., op. cit., p. 5.

the original. Although these observations indicate no measurable inversion interval the broken curve *KX* has been added to the diagram to indicate a very small inversion interval, in order that the diagram as a whole may have the theoretical form that makes it the more intelligible.

Other Solid Phase Relations of Metasilicate Compositions.

Of the changes taking place in the solid state depicted in Fig. 8 the transformation represented by the curves *KY* and *KX* alone is of binary character. The ternary equilibrium indicated by the curve *CY* is concerned with the initial break-down of the clino-pyroxene into olivine and tridymite upon heating. The curve *CY* is located partly by the use of pure synthetic preparations and partly by the use of natural minerals. Thus the mixture $MgSiO_3$ 30 $FeSiO_3$ 70 can be crystallized to a homogeneous clino-pyroxene at temperatures of 1050°-1100°, and if the product is heated at a temperature just above 1150° dissociation takes place with formation of some olivine and tridymite. They appear first as minute crystals of refractive index different from that of the enclosing pyroxene.

Likewise if the natural hypersthene from Tunaberg, Sweden, which is transformed into clino-hypersthene at 955°, be heated only about 5° above that temperature, dissociation of the clino-pyroxene into olivine and tridymite begins.

As a result of such observations the curve *CY* is located, and since its position is based partly upon determinations with pure synthetic preparations, and these are in general agreement with those made upon natural material, it would appear that no great change of solid phase equilibrium is introduced by the presence of the foreign oxides in the natural minerals. Again, the fact that curves *CY* and *KY* come together at *Y* in the appropriate manner suggests that although portions of these curves were determined with the aid of natural minerals the position of the curves on the actual diagram for pure iron-magnesium silicates would not be significantly different and that we are justified in presenting the diagram so determined as that of the pure iron-magnesium silicates.

It was only for some of these low temperature equilibria that it was necessary to resort to the use of natural minerals. All other curves are fixed with the aid of pure synthetic mixtures.

Cooling of Metasilicate Mixtures from the Liquid State.

The manner in which Fig. 8 can be put to use may be brought out by the discussion of the cooling of typical liquids, the attainment of perfect equilibrium being assumed.

A liquid of composition $MgSiO_3$ 90 $FeSiO_3$ 10 begins to crystallize at 1555° with separation of olivine, whose composition cannot be read from the diagram. The olivine continues to crystallize until a temperature of 1545° is attained, when there begins separation of clino-pyroxene of composition $MgSiO_3$ 98 per cent. With further cooling clino-pyroxene separates and olivine is resorbed, until at 1527° the olivine has completely disappeared. The pyroxene now has the composition *B* and the liquid the composition *O* and henceforth the behavior is binary. With further cooling the pyroxene increases in amount and changes in composition along *BS*, while the composition of the liquid changes along *OR*, until at 1500° the pyroxene has the composition $MgSiO_3$ 90 $FeSiO_3$ 10 and the last trace of liquid, now of composition $MgSiO_3$ 70 $FeSiO_3$ 30, vanishes. If the clino-pyroxene is now further cooled it should, if equilibrium were reached, be transformed completely into ortho-pyroxene at 1140°.

The liquid $MgSiO_3$ 70 $FeSiO_3$ 30 begins to crystallize at 1500° with separation of crystals of $MgSiO_3$ 90 $FeSiO_3$ 10. As the temperature falls the crystals change in composition along *BS* and the liquid along *OR* until at 1415° the crystals have the composition $MgSiO_3$ 70 $FeSiO_3$ 30 and the last trace of liquid, now of composition $MgSiO_3$ 45 $FeSiO_3$ 55, vanishes. If the clino-pyroxene is now cooled to 1110° it should invert into the orthorhombic form if equilibrium were reached. The behavior is thus strictly binary throughout.

The liquid $MgSiO_3$ 50 $FeSiO_3$ 50 begins to crystallize at 1440° with separation of crystals of clino-pyroxene $MgSiO_3$ 75 $FeSiO_3$ 25. Upon cooling, the crystals increase in amount and change in composition along *BS* and the liquid changes along *OR* until at 1400° the liquid has the composition *R* and the crystals the composition *S*. Separation of tridymite now begins and crystallization ceases to be binary. Pyroxene and tridymite crystallize through a small interval of temperature and then tridymite begins to be resorbed, until at 1340° the last of the tridymite and of the liquid disappear simultaneously and the charge consists wholly of clino-pyroxene of composition $MgSiO_3$ 50 $FeSiO_3$ 50. Upon cooling to 1085° the clino-pyroxene would invert to ortho-pyroxene if equilibrium were attained.

The liquid $MgSiO_3$ 30 $FeSiO_3$ 70 begins to crystallize at 1455° with separation of tridymite and crystallization is of ternary character throughout. At 1350° tridymite is joined by pyroxene which continues to separate until 1305°, when it reacts with liquid to produce olivine and tridymite, the temperature remaining constant until all the pyroxene has disappeared. Further crystallization of olivine and tridymite then occurs until the liquid has entirely disappeared at 1295°. The crystalline aggregate of olivine and tridymite remains as such until 1285°, where reaction between them begins, with resultant formation of clino-pyroxene. This reaction continues until the temperature reaches 1150°. Combination is then complete and the mass consists entirely of clino-pyroxene of composition $MgSiO_3$ 30 $FeSiO_3$ 70. Upon cooling the clino-pyroxene to 1020° it would be transformed into ortho-pyroxene if equilibrium were reached.

The liquid $MgSiO_3$ 10 $FeSiO_3$ 90 begins to crystallize at 1530° with separation of cristobalite which continues to form until 1470°, where it is transformed into tridymite. Tridymite continues to separate until the temperature has reached 1240°, when olivine forms in addition, and the two crystallize until the temperature is 1220°, when crystallization is complete. Cooling to 1010° results in the beginning of reaction between olivine and tridymite to form clino-pyroxene which continues down to 955°. At this temperature the clino-pyroxene, now of composition Y, is transformed into ortho-pyroxene of composition X and the crystalline aggregate of olivine, tridymite, and ortho-pyroxene persists indefinitely at lower temperatures except that at 870° tridymite is transformed to quartz.

A SERIES OF ISOTHERMAL PLANES.

The salient features of the equilibrium relations of the metasilicate and of the orthosilicate solid solutions, individually, have now been pointed out. Although some aspects of the relations between the two series have been brought out by means of the metasilicate section, a complete picture of the composition of all the phases concerned in the equilibria is gained only with the aid of ternary figures. We shall therefore present a series of isothermal planes.[15]

---

[15] These figures, representing isothermal planes, are all drawn to true scale, the composition of all phases (including the solid solutions but excepting the magnesio-wüstites) being determined by the experimental results. Further information regarding these determinations is given under the head "Three Phase Triangles and Three Phase Boundaries."

The first to be discussed is that for 1550°, Fig. 9. At this temperature the liquid *a*, which is of orthosilicate composition, is in equilibrium with olivine whose composition lies at the point at the other end of the brace joining it with *a*. The equilibrium is binary, the brace being the device here adopted to indicate binary equilibrium. All the liquids *a-b* are in equilibrium with olivine, each with an olivine of different composition as indicated by the tie-lines. Any mixture whose composition is represented by a point in the triangle *aob* thus consists at 1550° of olivine and liquid, the composition of each of which is indicated by the ends of the tie-line passing through the point of composition of the mixture.

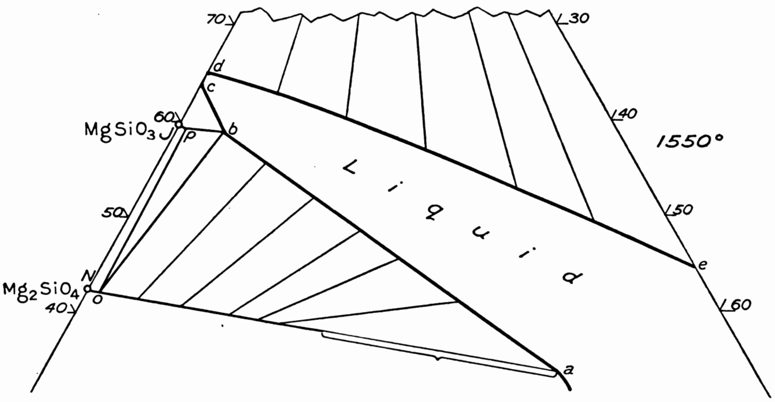

Fig. 9. Phase relations at 1550°. Truncated SiO_2 apex = *T* in text. Cf. Fig. 11.

The liquid *b* is in equilibrium with both the olivine *o* and the pyroxene *p* and is therefore a point in the boundary curve *KL* of Fig. 5. All mixtures lying in the triangle *pbo* consist at 1550° of the three phases, liquid *b*, pyroxene *p*, and olivine *o*.

The liquids *b* to *c* are in equilibrium with clino-pyroxenes varying in composition from *p* to *J* and all mixtures in the area *cbpJ* thus consist at 1550° of liquid between *b* and *c* and pyroxene between *p* and *J*. Tie-lines are here omitted to avoid crowding.

The mixtures in the area *JpoN* are completely crystalline at 1550° and consist of pyroxene *p* to *J* and olivine *N* to *o*.

The liquids *d* to *e* are in equilibrium with cristobalite at 1550° and all mixtures in the triangle *deT* consist at 1550° of cristobalite and liquid whose composition is given by the tie-line passing through the point indicating the total composition of the mixture. The tie-lines are thus lines radiating from the SiO_2 apex here truncated to save space, but called *T* in this and subsequent figures.

The next isothermal plane (Fig. 10) is that for 1527°, the temperature of the point *O* of Fig. 5 at which the metasilicate join crosses the pyroxene-olivine boundary curve. The point is lettered *O* in Fig. 10 also. It is not an invariant point but is merely a limiting case of points having the properties of *b* in Fig. 9. The liquid *O* is in equilibrium with the pyroxene *p* (a binary relation indicated by a brace) and also with the olivine *o*. The liquids *O* to *c* are in equilibrium with pyroxenes *p* to *p′*. The liquid *c* is in equilibrium with the pyroxene *p′* and with cristobalite. All mixtures in the triangle *cp′T* consist of the three phases pyroxene *p′*, cristobalite, and liquid *c*. All mixtures in the triangle *p′JT* consist of the two phases cristobalite and a pyroxene between *p′* and *J*. All other areas have the same properties as their analogues in Fig. 9.

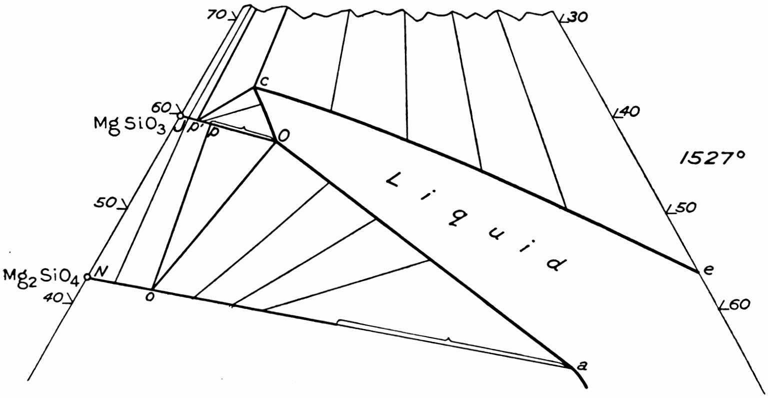

Fig. 10. Phase relations at 1527°. Truncated SiO_2 apex = *T* in text.

The next isothermal plane, Fig. 11, is that for 1450°. All other figures of this character have been limited on the low-silica side by the orthosilicate join and have been truncated on the high-silica side. In the present example the full triangle is shown in order to make clear the general appearance of the completed figures. This particular temperature is so treated because it is the only one at which the equilibrium involving magnesio-wüstite has been approximately determined.

The liquids *f* to *g* are in equilibrium with magnesio-wüstites and the liquid *f* is in equilibrium with both magnesio-wüstite *h* and olivine *o′*. The liquids *f* to *a* to *b* are in equilibrium with olivines.

One special feature may be pointed out. At 1527° (see Fig. 10) the pyroxene *p′*, which is in equilibrium with SiO_2 and liquid, is more magnesian than the pyroxene *p*, which is in equilibrium with olivine and liquid. At 1400° (see Fig. 12) the opposite condition prevails, i.e., the pyroxene *S*, which is in equilibrium with SiO_2 and liquid, is less magnesian than the pyroxene *p*, which is in equilibrium with olivine and liquid. At some intermediate temperature, therefore, SiO_2 and liquid on the one hand and olivine and liquid on the other will be in equilibrium with the same pyroxene. Our determinations do not enable us to state definitely the temperature at which this condition prevails, but they indicate that it is probably not far from 1450°. In Fig. 11, therefore, the liquid *c* and SiO_2

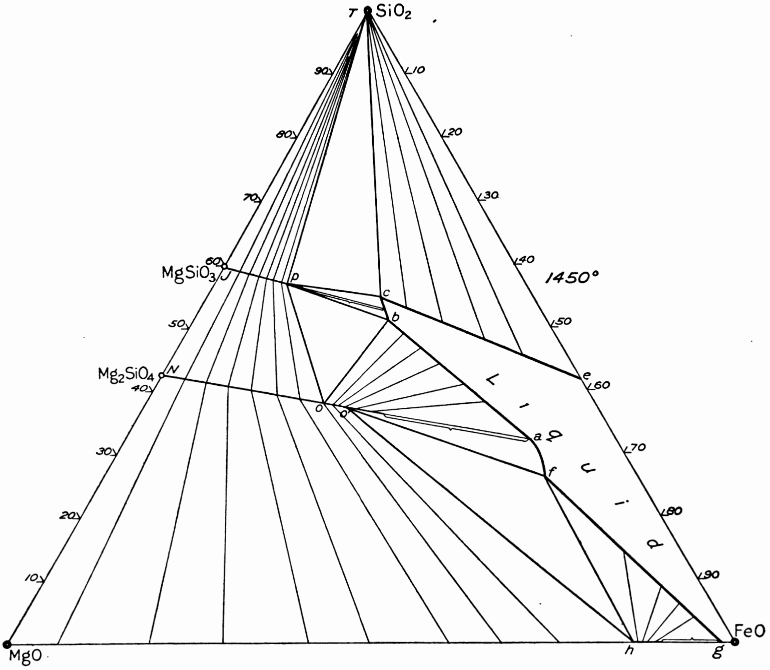

Fig. 11. Phase relations at 1450°.

(tridymite) and also the liquid *b* and olivine *o* are shown in equilibrium with the same pyroxene *p*.

The next isothermal plane (Fig. 12) is that for the temperature 1400°, the temperature of the point *R* of Figs. 5 and 8, which is not an invariant point but merely the point of intersection of the pyroxene-tridymite boundary curve with the metasilicate join. The liquid *R* is in equilibrium with the pyroxene *S* (the binary relation indicated by the same letters in Fig. 8) and with tridymite. All other areas have the properties of their analogues in former figures.

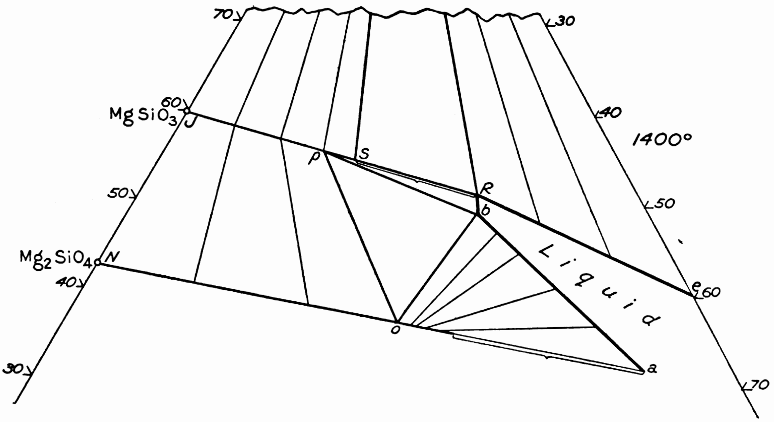

Fig. 12. Phase relations at 1400°. Truncated SiO$_2$ apex = *T* in text.

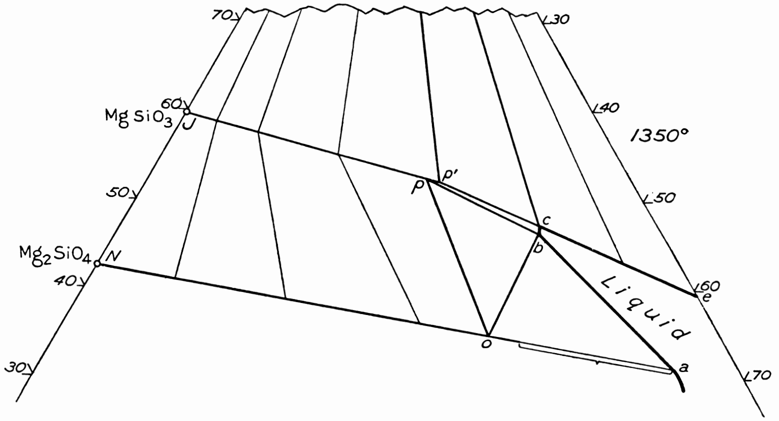

Fig. 13. Phase relations at 1350°. Truncated SiO$_2$ apex = *T* in text.

The next isothermal plane (Fig. 13) is that for 1350°, which

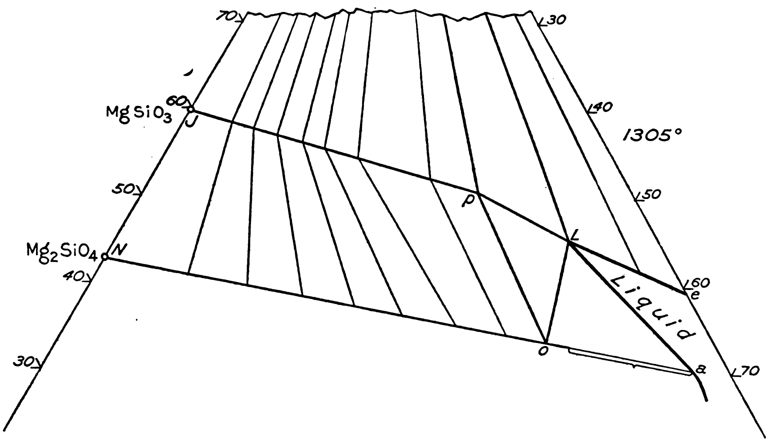

Fig. 14. Phase relations at 1305°. Truncated SiO_2 apex $= T$ in text.

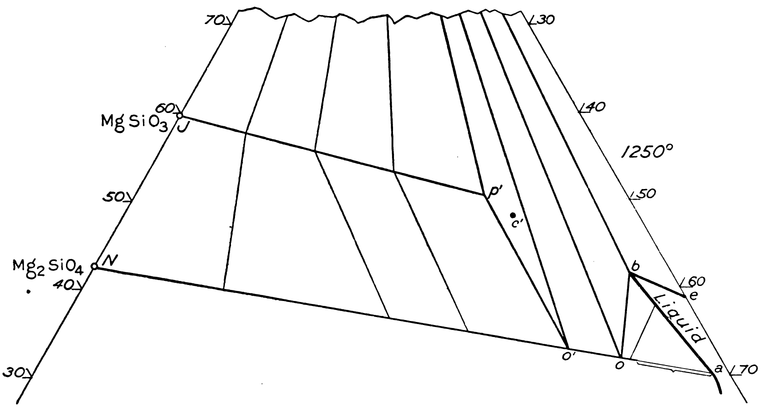

Fig. 15. Phase relations at 1250°. Truncated SiO_2 apex $= T$ in text.

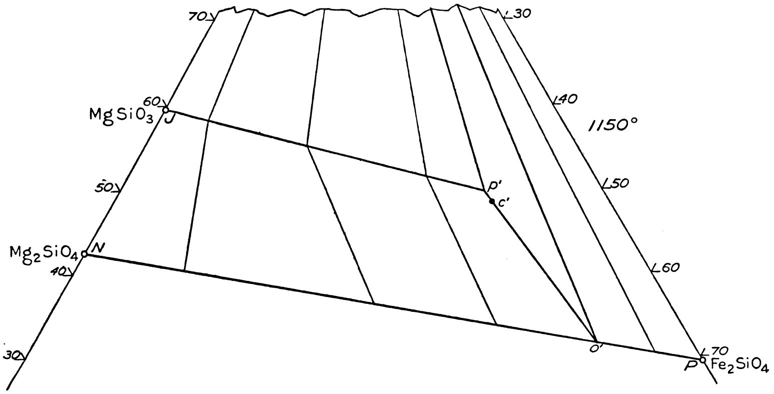

Fig. 16. Phase relations at 1150°. Truncated SiO_2 apex $= T$ in text.

is typical of those temperatures between 1400° and 1305° where both the liquid *c*, in equilibrium with pyroxene *p′* and tridymite, and the liquid *b*, in equilibrium with the pyroxene *p* and olivine *o*, lie on the low-silica side of the metasilicate join. The areas require no special discussion.

The next isothermal plane (Fig. 14) is that for 1305°, the temperature of the invariant point *L* of Fig. 5 which is again lettered *L* in the present figure. The liquid *L* is in equilibrium with the three solid phases with which it is joined, viz., olivine *o*, pyroxene *p*, and tridymite *T*. At a temperature immediately below 1305°, pyroxene ceases to be stable in contact with liquid. The line *pL* therefore disappears and its place is taken by *oT*.

The next isothermal plane (Fig. 15) is that for 1250°, typical of those temperatures where only olivine and tridymite are in equilibrium with liquid. The liquid *b* is that in equilibrium with both these phases, the olivine having the composition *o*. The triangle *boT* includes the composition of all mixtures that consist of the three phases, liquid *b*, olivine *o*, and tridymite *T*. The adjacent triangle *oo′T* includes all mixtures that consist of only the two phases, tridymite *T* and an olivine between *o* and *o′*. The triangle *o′p′T* is again a three-phase triangle, in this instance all three phases being solid, the olivine *o′*, the pyroxene *p′*, and tridymite *T*.

The next isothermal plane (Fig. 16) shows the relations at 1150°, a temperature at which no liquid forms in any mixture of the system. There is only one three-phase triangle, the three-solid-phase triangle *o′p′T* which includes all mixtures that consist of the three phases, olivine *o′*, pyroxene *p′*, and tridymite *T*.

The next isothermal plane (Fig. 17) is that for 1050°, typical of temperatures where two different kinds of pyroxene co-exist in equilibrium. The triangle *o″p″p‴* is a three-solid-phase triangle which includes all mixtures that consist of olivine *o″*, ortho-pyroxene *p″*, and clino-pyroxene *p‴*. The three-solid-phase triangle *p″p‴T* includes all mixtures that consist of the same two pyroxenic phases and tridymite. The three-solid-phase triangle *o′p′T* has the same properties as its analogue in Figs. 15 and 16. All other areas are two-phase areas. Thus the area *JNo″p″* includes all mixtures that consist of the two phases, olivine between *o″* and *N* and ortho-pyroxene between *p″* and *J*. The area *o″o′p′p‴* includes all mixtures that consist of the two phases, olivine between

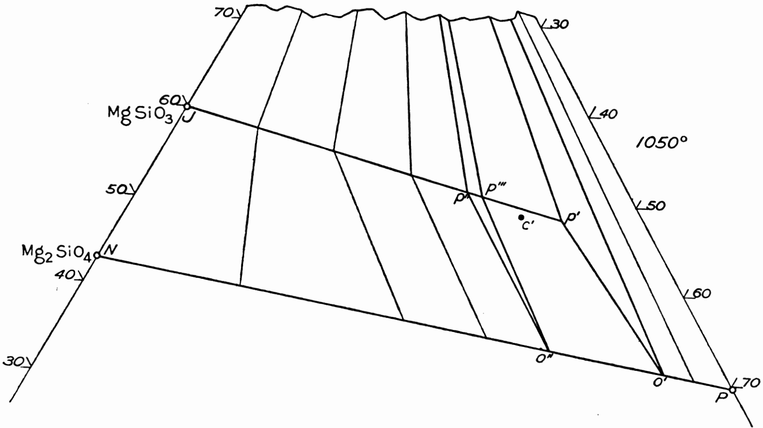

Fig. 17. Phase relations at 1050°. Truncated SiO_2 apex = T in text.

o'' and o' and clino-pyroxene between p''' and p'. With this explanation no discussion of the other areas is necessary.

The next isothermal plane (Fig. 18) is that for 955°, which is the temperature of the invariant point at which four solid phases coexist, the horizontal XYZ of Fig. 8. The points X and Y of Fig. 18 correspond with the points similarly lettered in Fig. 8. The four solid phases in equilibrium are ortho-pyroxene X, clino-pyroxene Y, olivine o, and tridymite T. This temperature is the lowest temperature of stable existence of pure ferromagnesian clino-pyroxene. Immediately above 955° the triangle TYo represents the stable configuration. Immediately below 955° the triangle TXo represents the stable configuration.

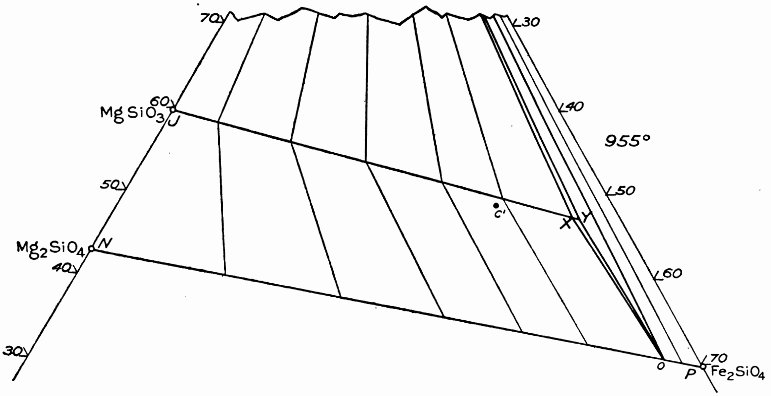

Fig. 18. Phase relations at 955°. Truncated SiO_2 apex = T in text.

THREE-PHASE TRIANGLES AND THREE-PHASE BOUNDARIES.

In the isothermal figures there are numerous examples of liquids that are in equilibrium with two solid phases. The point indicating the composition of the liquid is the apex of a three-phase triangle, the two points at the ends of the base indicating the composition of the two solid phases. The sides of a three-phase triangle are called three-phase boundaries and are to be carefully distinguished from boundary curves. The three-phase triangles referring to the equilibrium between liquid, olivine, and pyroxene are of greatest interest in the present system. These are the triangles *bop* of Figs. 9-14.[16] It is important to note that any point in the three-phase boundary *bo* of any one of these figures represents a mixture which consists of liquid *b* and olivine at the temperature at which the individual diagram applies. Any such mixture cooled from the liquid state has therefore experienced separation of olivine and has just arrived at a temperature where separation of pyroxene begins. Similarly, any mixture represented by a point in the three-phase boundary *bp* consists of liquid and pyroxene and has just arrived at a temperature where separation of olivine begins. Moreover, any point in the three-phase boundary *op* (the base of the three-phase triangle) of these several figures represents a mixture consisting of pyroxene *p* and olivine *o* and, if cooling, has just reached that condition, i.e., the last trace of liquid has just disappeared. Obviously it is necessary to know the position of these three-phase boundaries in order to be able to describe accurately the course of crystallization of any mixture. One method of determining these three-phase boundaries is to hold a mixture at a temperature at which it consists of liquid with some olivine and pyroxene crystals and to determine optically the composition of both olivine and pyroxene. This gives the two points at the ends of the base of the three-phase triangle. Since the composition of the liquid lying on the boundary curve at all temperatures has been previously determined, the apex of the three-phase triangle for the temperature of the experiment is known and therefore the complete triangle. Such determinations have been made upon a number of mixtures at different temperatures. It is with these as basis and, of course, similar determinations for other types of

---

[16] There is no triangle *bop* in either Fig. 10 or Fig. 14, but the triangles *Oop* and *Lop* of these figures respectively are limiting cases of the triangle *bop* and have the same properties.

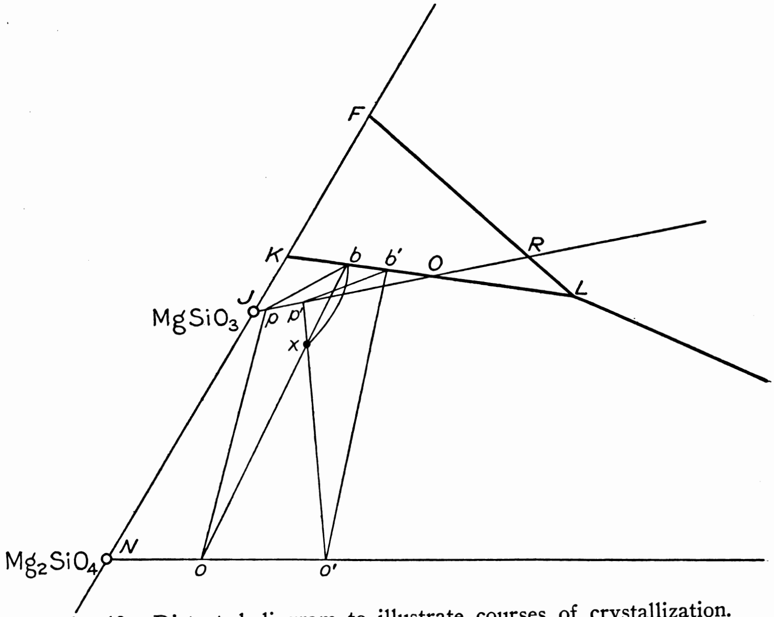

Fig. 19. Distorted diagram to illustrate courses of crystallization.

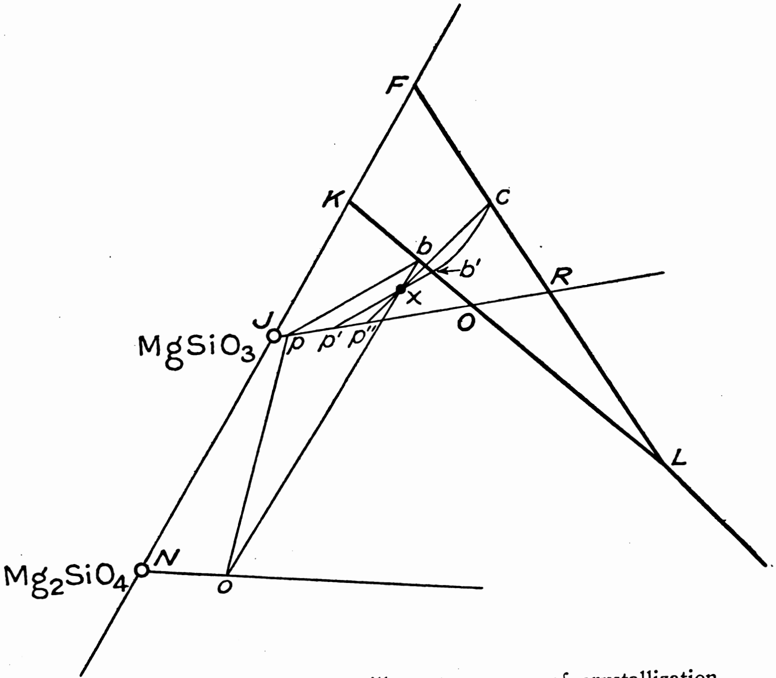

Fig. 20. Distorted diagram to illustrate courses of crystallization.

three-phase triangles, that the several isothermal figures 9-18 have been drawn. They are drawn to scale and solid-phase compositions may be read from them. No table of such compositions is given, since they do not lend themselves to presentation in such form.

A more extended discussion of the general properties of three-phase triangles is given in the paper on the system, CaO-FeO-SiO_2.[17]

COURSES OF CRYSTALLIZATION.

With this preliminary explanation of the method of determination and of the full significance of the three-phase boundaries of the isothermal figures, we may proceed to discuss the crystallization of typical liquids. For this purpose it is, in some instances, necessary to use a distorted diagram on account of the confusion of lines and points that would otherwise result. Fig. 19 is such a distorted diagram on which the several points and curves have been lettered in accordance with the plan used in the isothermal figures 9-18. A mixture of composition x (Fig. 19) begins to crystallize with separation of a highly magnesian olivine of composition represented by a point between o and N. The liquid follows the curved course xb,[18] reaching the boundary curve KL at b when the olivine has attained the composition o, the line ob being the three-phase boundary (of the ob type of Figs. 9-14) which passes through x. At the temperature of b pyroxene of composition p begins to crystallize, bp being a three-phase boundary of the bp type of Figs. 9-14. With further cooling the liquid changes along the boundary curve KL, pyroxene separating and olivine being resorbed and both being changed continuously in composition. At b' the last trace of liquid disappears, $o'p'$ being the base of the three-phase triangle or the three-phase boundary (of the op type of Figs. 9-14) which passes through x, and b' being its apex. The mass then consists entirely of pyroxene p' and olivine o'. The pyroxene which forms directly from liquid is in all mixtures of this system, clino-pyroxene. Upon cooling it is transformed, at equilibrium, to ortho-pyroxene but we shall not follow the majority of the mixtures discussed beyond the stage where they first become completely crystalline. On a later page the

---

[17] Bowen, N. L., Schairer, J. F., and Posnjak, E.: Op. cit., p. 233 ff.

[18] Necessarily curved because the composition of the olivine is continually moving along No towards o.

changes in the solid state will be followed for one mixture, by way of illustration of the use of three-solid-phase triangles.

The mixture x of Fig. 19 is typical of those that exhibit partial but incomplete resorption of olivine. We shall now discuss a mixture which is typical of those that exhibit complete resorption of olivine. The mixture x of Fig. 20 (also a distorted diagram) is of this latter character. Cooled from the liquid state, it precipitates olivine first and the composition of the liquid follows a curved course to the boundary curve KL at b, at which time the olivine has the composition o. Pyroxene of composition p then begins to separate and the liquid moves along the boundary curve, pyroxene separating and olivine being resorbed. When the liquid has reached the composition b', such that the three-phase boundary $p'b'$ passes through x, the mixture now consists only of pyroxene p' and liquid, i.e., the olivine has been completely resorbed. The liquid

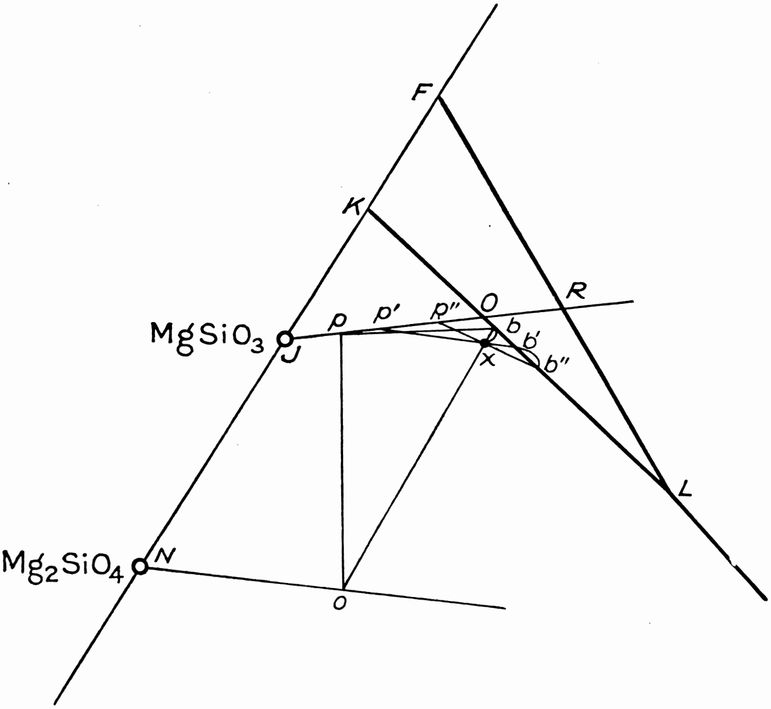

Fig. 21. Distorted diagram to illustrate courses of crystallization.

now crosses the pyroxene field on the curved course $b'c$. At c the pyroxene has the composition p'', the line $p''c$ being a three-phase boundary of the type $p'c$ of Figs. 10 and 11.[19] From the liquid c cristobalite begins to separate and the liquid changes along the boundary curve towards R, both pyroxene and cristobalite separating until the liquid is exhausted, at which time the liquid has a composition between c and R not far removed from c. The actual point and the construction lines that determine it are not given on account of the confusion of lines that results, but it is the apex of the three-phase triangle (of the type of cpT of Fig. 11) whose base (of the type Tp of Fig. 11) passes through x.

The liquid x of Fig. 21 is typical of a small area of liquids in the angle JOL of Fig. 5. Again a distorted diagram is necessary. Crystallization begins with separation of olivine and the liquid follows the curved course xb. When the liquid has the composition b the olivine has the composition o and pyroxene of composition p begins to separate. The liquid now moves along the boundary curve towards L, pyroxene separating and olivine being resorbed. When the liquid has reached the composition b', whose position is determined by the three-phase boundary (of the pb type of Figs. 9 and 10) which passes through x, the pyroxene has the composition p' and the olivine is completely resorbed. The liquid now leaves the boundary curve and moves into the pyroxene field, pyroxene alone separating. The liquid follows the curved course $b'b''$ which brings it back to the boundary curve at b''. The position of b'' is determined by another three-phase boundary (also of the pb type of Figs. 9 and 10) which passes through x. Olivine now begins to crystallize again and separates together with pyroxene until crystallization is complete. The last minute quantity of liquid has the composition represented by a point on the boundary curve between b'' and L (not indicated in the diagram), the position of the point being determined as the apex of the three-phase triangle (of the type bpo) whose base (of the type po) passes through x. Only a very small area of liquids represented by points in the angle JOL have two different three-phase boundaries of the pb type passing through them, and the range of liquids which show this precipitation, complete resorption, and reprecipitation of olivine is therefore much restricted. There is, however, a considerable range of composition of liquid, of which points

---

[19] In Fig. 11 p and p' fall at one point which is lettered p.

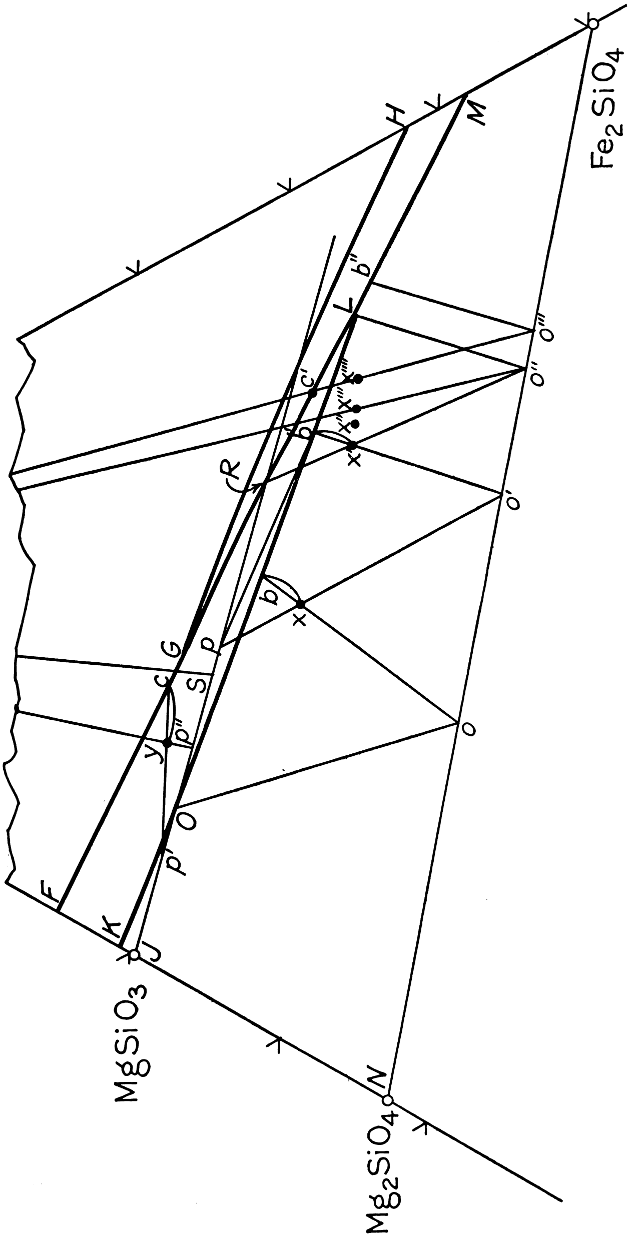

Fig. 22. True-scale diagram to illustrate courses of crystallization.

in *bo* between *x* and *o* are representative, that shows incomplete resorption of olivine followed by a period of renewed precipitation of olivine.

The crystallization of a great many liquids can be discussed satisfactorily with the aid of an undistorted or true-scale diagram. Fig. 22 is of this character. With its aid we may discuss the crystallization of a number of mixtures in the olivine field which have characteristics somewhat different from those of mixtures in that field that have already been discussed. The liquid *x* begins to crystallize with separation of olivine and follows the curve *xb*. When the liquid has the composition *b* the olivine has the composition *o* and pyroxene of composition *O* begins to crystallize. Not only pyroxene but olivine also continues to separate (no resorption of olivine) the liquid following the boundary curve to *b′* when the pyroxene has the composition *p*, the olivine the composition *o′*, and the last trace of liquid has just disappeared (since *po′* passes through *x*). Mixtures lying in the three-phase boundary *ob* (of which *x* is typical) are the first mixtures that fail to show resorption of olivine, i.e., all mixtures to left of *ob* in the olivine field do show resorption of olivine whereas all mixtures to the right do not. The reason for this situation is that liquids to the right of *b* on the boundary curve are in equilibrium with olivine and with a pyroxene to the right of *O*, on the metasilicate join, that is, with two solid phases that lie on opposite sides of the boundary curve,[20] and movement along the boundary curve is accomplished by subtraction of both these solid phases. On the other hand, liquids to the left of *b* on the boundary curve are in equilibrium with olivine and with a pyroxene to the left of *O*, i.e., between *J* and *O*. They are thus in equilibrium with two solid phases that lie on the same side of the boundary curve and movement along the boundary curve can thus be accomplished only with resorption of the olivine and separation of pyroxene. Because all mixtures to the right of *ob* show only simple subtraction of both olivine and pyroxene from the liquid and all liquids to the left of *ob* show, at some stage, resorption of olivine, it is not to be assumed that liquids to the left of *ob* never show simple subtraction of both olivine and pyroxene. Some of them do in the final stages of their crystallization,

---

[20] Since the boundary curve is sensibly a straight line there is no need to speak of the tangent to it.

as we have seen in the discussion of mixtures referred to Fig. 21.

The mixture *x′* of Fig. 22 begins to crystallize with separation of olivine, and the liquid follows the curved course *x′b′*. At *b′* the olivine has the composition *o′*, pyroxene of composition *p* begins to separate, and the liquid moves along the boundary curve to *L*. At *L* the olivine has the composition *o″* and the pyroxene a composition, for all practical purposes, coincident with *R*. Since *o″R*, the base of the three-phase triangle, passes through *x′*, the mass consists entirely of the two solid phases, and the liquid, now of composition *L*, has vanished.

The mixtures *x″*, *x‴* and *x⁗* will, of course, still have some liquid of composition *L* when they reach the temperature *L* because they lie within the three-phase triangle *Ro″L*. The liquid *L* will then react with pyroxene to produce olivine and tridymite, the temperature remaining constant meanwhile. In the case of mixture *x″* the liquid will be consumed by this reaction and the completely crystalline mass will consist of olivine *o″*, pyroxene *R* and tridymite *T*. In the case of mixture *x‴* pyroxene and liquid are exhausted simultaneously and the mass consists of olivine *o″* and tridymite *T*. In the case of mixture *x⁗* some liquid remains when the pyroxene is consumed. The liquid changes in composition along *LM*, olivine and tridymite separating. Crystallization is complete when the liquid has reached the composition *b″* and the olivine the composition *o‴*, the base *o‴T* of the three-phase triangle *b″o‴T* passing through *x⁗*.

The olivine *o″* is plainly the most magnesian olivine that can form in equilibrium with free silica in the present system at atmospheric pressure. It has about 32 per cent Mg_2SiO_4.

We may now turn to the crystallization of liquids in the pyroxene field. The liquid *y* of Fig. 22 begins to crystallize with separation of pyroxene of composition between *p′* and *J* and the liquid follows the curved course *yc* to the boundary curve. When the liquid has the composition *c* the pyroxene has the composition *p′* and cristobalite begins to separate, *p′c* being the three-phase boundary of the type so lettered in Fig. 10. The liquid then moves along the boundary curve with separation of both pyroxene and cristobalite until the liquid has the composition *G*, when cristobalite changes to tridymite. The liquid then moves along the boundary curve *GL* and is finally consumed when it has a composition represented by a point not far from *G*. The position of the point is determined as the apex of the three-phase triangle (of the *pTc* type of Fig. 11) whose base (of the *pT* type of Fig. 11) passes through *y*.

No other mixtures in the pyroxene field will be discussed except those that show features of particular interest. Among these are included all mixtures whose crystallization is such that at some stage the liquid moves along the portion *RL* of the boundary curve *GRL*. A distorted diagram, Fig. 23, is necessary for the discussion of these. In it curves are lettered to correspond with those in the undistorted diagram (Fig. 22) and the relations depicted are readily transferred mentally to the undistorted figure.

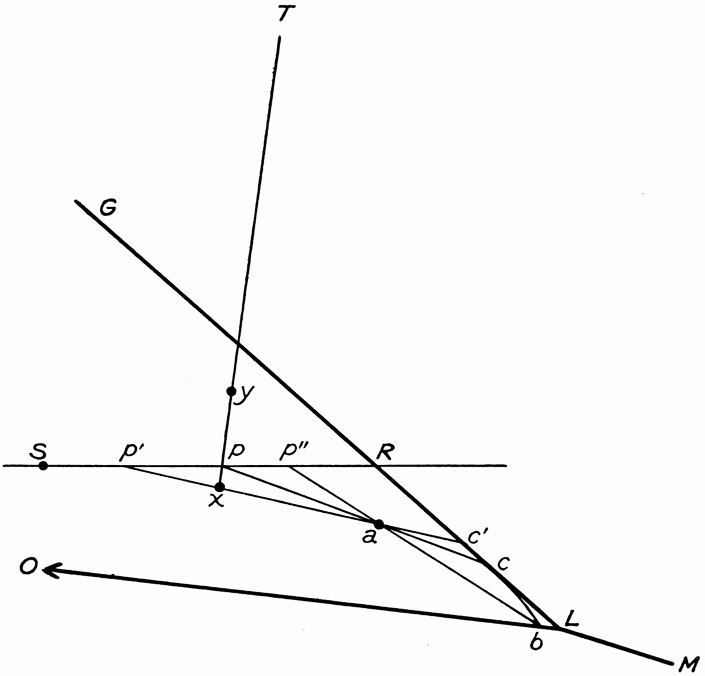

Fig. 23. Distorted diagram to illustrate courses of crystallization.

The mixture *p* of Fig. 23 is of metasilicate composition. Its crystallization can therefore be read from Fig. 8 but not in full detail, for at certain stages the equilibrium is ternary and the composition of some phases appearing at these stages is incapable of expression in Fig. 8. In Fig. 23, on the other hand, all phases can be depicted. Thus the liquid p begins to crystallize with separation of clino-pyroxene somewhat more magnesian than S and the liquid, maintaining metasilicate composition, moves along pR to R, at which temperature the crystals have the composition S. Now crystallization of tridymite begins and the liquid follows the boundary curve RL. When the liquid has attained the composition c' the pyroxene has the composition p', $c'p'$ being a three-phase boundary of the type cp' of Fig. 13. The proportions of the three phases, liquid c', pyroxene p', and tridymite T are determined by the position of the point p within the three-phase triangle $p'c'T$. In particular the proportion of tridymite is given by the ratio $\frac{px}{Tx}$, x being the point of intersection of $p'c'$ and Tp produced. When the liquid has attained the composition c, the pyroxene has attained the composition p, cp being again a three-phase boundary of the same type. But since p lies in the base pT of the three-phase triangle the liquid is reduced to zero when it has attained the composition c and, since p lies at the end of the base, the tridymite is likewise reduced to zero. Thus both tridymite and liquid are finally consumed when the liquid has the composition c and the whole mass then consists of the pyroxene p. As the liquid changes from R to c there is, then, at first an increase of tridymite from its initial value of zero, passage through a maximum value and then final return to zero. The maximum proportion of tridymite will obviously occur when the value of the intercept px and therefore of the ratio $\frac{px}{Tx}$ passes through a maximum as the three-phase boundary passes from the position SR, through $p'c'$, to the position pc.

The crystallization of the liquid y is in some respects related to that of the liquid p. Crystallization begins with the separation of pyroxene somewhat more magnesian than S. The liquid follows a curved course to the boundary curve GR where crystallization of tridymite begins. The liquid then moves along the boundary curve with separation of both tridymite and pyroxene. When the liquid has the composition R (1400°) the pyroxene has the composition S, and the third phase is tridymite T. The proportion of tridymite at this temperature is given by the ratio $\frac{yp}{Tp}$. With further cooling the liquid moves towards L. When it has attained the composition c', the pyroxene has the composition p' and the proportion of tridymite is given by the ratio $\frac{yx}{Tx}$, which is greater than $\frac{yp}{Tp}$. When the liquid attains the composition c, the pyroxene has the composition p. The amount of liquid has therefore been reduced to zero and the mass consists entirely of tridymite T and pyroxene p. The proportion of tridymite is again $\frac{yp}{Tp}$, the same as it was at 1400°. During the fall of temperature and change of composition of liquid from R to c the proportion of tridymite plainly passes through a maximum and this maximum is at the same temperature as that for the liquid p already discussed, since it likewise depends on the maximum value of the changing intercept xp, or more specifically xy, which is xp plus the constant yp.

From the above discussion it will be clear that for all mixtures on the three-phase boundary Tp there is a certain temperature and composition of the liquid between R and L at which the proportion of tridymite passes through a maximum, i.e., separation of tridymite ceases and its resorption begins. Moreover, this is the same temperature (and composition of the liquid) for all these mixtures lying in Tp. For any other mixture such as p' or one lying in $p'T$ there is likewise a temperature of maximum proportion of tridymite but it is a different temperature (and composition of the liquid) from that obtaining for mixtures lying in pT. Thus the reaction that takes place *at any point* in the curve RL may be different for different total compositions of the mixtures concerned, that is, for different proportions of the three phases concerned, the compositions of the individual phases being necessarily the same in all cases. At a certain temperature tridymite will be *subtracted from* the liquid if the total composition (in other words the relative proportions of the three phases) has a certain value, and at the same temperature tridymite will be *added to* (resorbed by) the liquid if the proportions have a certain different value.

There is yet another type of mixture whose course of crystallization falls, in part at least, along the portion RL of the boundary curve. The metasilicate mixture p and the mixture y with excess silica over the metasilicate ratio have been discussed. We shall now turn to a mixture with a lower proportion of silica. Such a mixture is represented by a (Fig.

23). A liquid of composition *a* begins to crystallize with separation of pyroxene of composition approaching *S* and follows a curved course which meets the boundary curve at *c′*, the pyroxene then having the composition *p′*. At *c′* tridymite begins to separate and the liquid moves along the boundary curve. After a short period of separation, tridymite begins to be resorbed and when the liquid has the composition *c* resorption is complete, the mass consisting entirely of pyroxene *p* and liquid *c*. The liquid now leaves the boundary curve and passes across the pyroxene field on the curved course *cb* with continued separation of pyroxene until the boundary curve *OL* is encountered at *b*. Here olivine begins to separate, *bp″* being a three-phase boundary of the *bp* type of Fig. 13. With separation of both olivine and pyroxene the liquid moves along the boundary curve toward *L*. Further crystallization need not be discussed since it depends upon factors already considered in connection with the points *x′*, *x″*, *x‴*, and *x⁗* of the true-scale diagram, Fig. 22.

The liquid *a* (Fig. 23) is typical of those mixtures in the angle *SRL* through which pass two three-phase boundaries of the *pc* type.

It is to be noted that a liquid of the composition *c′*, when entirely free from crystals, moves along the boundary curve with separation of pyroxene and tridymite, passes through *c* still following the boundary curve, and effects resorption of tridymite which is not complete until the liquid has attained the composition *L*. The mass now consists of pyroxene *R* and liquid *L*, the ultimate three-phase boundary of the *pc′* type coinciding sensibly with *RL*. We may follow further crystallization of *c′* by referring back to the true-scale diagram, Fig. 22, upon which the composition *c′* has been marked. From this figure it is plain that the pyroxene *R* reacts with the liquid *L* to produce olivine *o″* and tridymite. In other words, tridymite, which had been completely resorbed, now reappears and the temperature remains constant at *L* until the pyroxene has disappeared. The liquid then moves along the boundary curve *LM* with separation of olivine and tridymite until the liquid has the composition *b″*, at which time crystallization is complete and the mass consists of olivine *o‴* and tridymite. Recapitulating, we find that tridymite appears, disappears, and reappears, pyroxene appears and disappears upon formation of olivine and tridymite from it, and if we follow the completely crystallized product to lower temperatures we find olivine and tridymite recombining to pyroxene. This is a truly remarkable complexity of behavior for a mixture of only three components.

Three-Solid-Phase Triangles.

We may illustrate the use of three-solid-phase triangles by following in detail the solid reactions taking place in the cooling mixture c' which we have already referred to in brief above. This may be done with the aid of Figs. 15-18 upon each of which the composition c' has been indicated. It will be noted that at 1250° (Fig. 15) the point c' lies in the three-solid-phase triangle $p'o'T$. The reaction between olivine and tridymite to produce pyroxene has, therefore, already gone on to a considerable extent.[21] At 1150° (Fig. 16) the point c' lies in the side $p'o'$ of the three-solid-phase triangle $p'o'T$. The reaction between olivine and tridymite has therefore just reached completion, tridymite being entirely consumed and the mass consisting mainly of pyroxene p' with a little olivine o'. At 1050° (Fig. 17) the point c' lies in the two-phase area $p'o'o''p'''$. The mass has experienced no change of condition from that obtaining at 1150° and still consists of the two phases olivine and clino-pyroxene. At 955° (Fig. 18) the point c' lies in the two-phase area $NJXo$. The mixture therefore consists of olivine and ortho-pyroxene, the change from clino- to ortho-pyroxene having occurred when the three-solid-phase triangle $p''p'''o''$ of Fig. 17 traversed the point c' in the migration of the triangle to the right with falling temperature.

Other Type of Three-Phase Triangle.

For completeness it is desirable to mention one other type of three-phase triangle necessary to the full description of equilibrium in the system. Three-phase triangles of this type refer to equilibrium in which two liquid phases and one crystalline phase are concerned. Cristobalite is the only crystalline phase that can occur in contact with two liquids, and the triangle valid for any given temperature has, therefore, as one apex the SiO_2 corner (A, Fig. 5) and as the other apices a point in BC and a point in DE representing the two liquids in equilibrium with each other at that temperature. Since the tie-lines crossing the area $BCED$ and joining liquids in equilibrium with each other are not determined, the details of such triangles cannot be pursued further.

---

[21] The reaction began, of course, when the side $o'T$ of the triangle $p'o'T$ passed through c' in its migration to the right with falling temperature.

OPTICAL PROPERTIES OF PHASES.

The identification of phases present in the product of any experiment is an essential part of an investigation of the kind here described. This was done by determining their optical properties with the aid of the petrographic microscope. A glassy phase was readily distinguished from crystals and the different kinds of crystals were distinguished from each other by exact measurements of optical constants. This permitted not only a determination of the phase but also, in the case of crystalline phases of variable composition (solid solutions), a rather close fixing of its composition. In order to determine the composition of a crystalline phase by optical means it is, of course, essential to know the manner of variation of optical properties with composition. Measurements must, therefore, be made upon crystals of known composition. These are best prepared by using a mixture of known proportions which can be induced to crystallize entirely to one phase, which phase will then necessarily have the composition of the mixture.

Magnesio-Wüstites.

The solid solutions between MgO and FeO are readily prepared by careful grinding together of Fe_2O_3, Fe powder, and MgO in the appropriate amounts to give the desired composition. The mixture is heated in a sealed, evacuated silica-glass tube at about 1200° for 48 hours. Fusion must be avoided and reaction permitted to occur between the solids. A thin skin of silicate forms at the contact of the preparation with the tube, but the main mass consists of minute crystals of a solid solution of MgO and FeO. These show a continuous variation of properties with composition. In color they vary, as powder, from pure white at the MgO (periclase) end, through pale yellow and brown to a black, opaque material at the FeO end. Even at 90 wt. per cent FeO a certain amount of brownish light is transmitted by very small crystals under the microscope. As far over as 78 per cent FeO enough light is transmitted to permit measurement of the refractive index in immersion media under the microscope, though the measurements are not of high accuracy in the iron-rich varieties. The results for sodium light are given in Table IV and Fig. 24.[22] It will be noted that when the composition is plotted in mol per cent the variation of refractive index is linear within the

---

[22] We are indebted to Dr. H. E. Merwin for special immersion media of high refraction and for guidance in their use.

limit of error of measurement. Extrapolation suggests a value of 2.32 for the refractive index of FeO.

TABLE IV.

Refractive Indices of Magnesio-Wüstites.

Composition				
wt. per cent		mol per cent		
MgO	FeO	MgO	FeO	Refractive index
100	..	100	..	1.736 ± .002
90	10	94.1	5.9	1.768 ± .002
75	25	84.3	15.7	1.822 ± .003
50	50	64.2	35.8	1.948 ± .005
21.9	78.1	33.3	66.7	2.12 ± .01

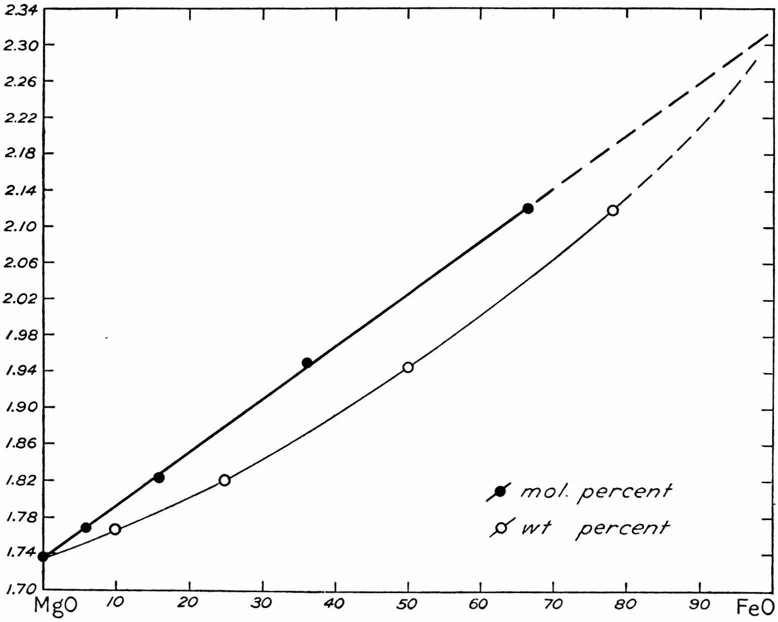

Fig. 24. Refractive indices of magnesio-wüstites.

Olivines.

Pure Mg-Fe olivines free from ferric iron and other oxides can be prepared by baking together for 48 hours MgO, Fe, Fe_2O_3, and SiO_2 in the proper proportions for the desired composition. This is accomplished in the absence of oxygen by sealing the mixed powders in an evacuated silica tube. Again fusion must be avoided and the reaction permitted to proceed between solids. The crystals of olivine prepared in this manner are rather minute but their refractive indices can be measured in immersion liquids under the microscope with considerable accuracy. The manner of variation of the refractive indices with composition in olivines has been the subject of a number of investigations. The natural minerals used, though permitting high accuracy of measurement, leave something to be desired because they contain small amounts of a number of different oxides whose individual effects are not readily made out. It is now 25 years since Backlund suggested that if the composition is plotted in molecular proportions the variation of refractive indices in Mg-Fe olivines is linear.[23] Natural olivines have not been of sufficient purity to permit the definite establishment of this relation but the synthetic olivines here prepared show that the relation is strictly true within the limit of error of measurement on the small crystals obtained. It is possible, of course, that some deviation from the linear relation could be made out if synthetic crystals large enough for plates and prisms were available. The results of the present measurements are given in Table V and in Fig. 25.

TABLE V.

Optical Properties of Synthetic Mg-Fe Olivines.

Composition						
wt. per cent		mol per cent		refractive indices		
Mg_2SiO_4	Fe_2SiO_4	Mg_2SiO_4	Fe_2SiO_4	γ	β	α
100	..	100	..	1.6688	1.6507	1.6359
75	25	81.3	18.7	1.709	....	1.671
50	50	59.2	40.8	1.752	1.738	1.712
25	75	32.6	67.4	1.807	1.794	1.762
10	90	13.9	86.1	1.848	1.835	1.798
..	100	..	100	1.875	1.864	1.824

---

[23] Backlund, Helge: Travaux du Musée Geologique Pierre le Grand, St. Pétersbourg Tome III, 77-105, 1909.

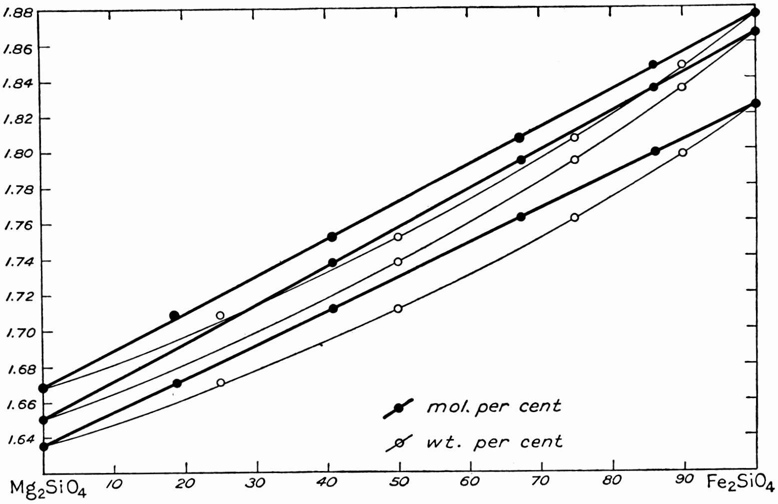

Fig. 25. Refractive indices of Mg-Fe olivines.

Pyroxenes.

Members of the $MgSiO_3$-$FeSiO_3$ series of pyroxenes were prepared in the present work in a form suitable for measurement of their refractive indices by devitrifying glasses of metasilicate composition. This procedure gave only clino-pyroxenes and although we occasionally obtained crystals of ortho-pyroxenes in our studies upon the transformation temperature, they were not suitable for the fixing of the variation of optical properties with composition in the orthorhombic pyroxenes. The clino-pyroxenes form an interesting series which extends over as far as about 87 per cent $FeSiO_3$. Those containing up to 70 per cent $FeSiO_3$ were prepared in the pure form by the method mentioned above. It is not possible to get homogeneous glasses richer in $FeSiO_3$, so beyond this point no pure synthetic clino-pyroxenes were made. It is possible, however, to prepare clino-pyroxenes of known composition from natural ortho-pyroxenes of known composition by simple inversion. This method was used in preparing the one clino-pyroxene with more than 70 per cent $FeSiO_3$. It was obtained by inversion of the Tunaberg ortho-pyroxene and of course contained all the extraneous oxides of the original mineral.

The clino-pyroxenes of the present series are all polysynthetically twinned on 100. They all have a small optic axial angle of about 20-25° positive and the plane of the optic axes is ⊥010. The extinction angle $c_{\wedge}\gamma$ rises from 22° in pure $MgSiO_3$ to 42° in the 60 per cent $FeSiO_3$ member and then falls off again to 36° in the extreme solid solution. The rise is so rapid with initial additions of $FeSiO_3$ that it was, at first, supposed that the extinction passed through 45° and that the smaller angles measured were complementary to $c_{\wedge}\gamma$, but careful work showed that this was not true and the passage of the extinction through a maximum was definitely established (see Fig. 26).[24]

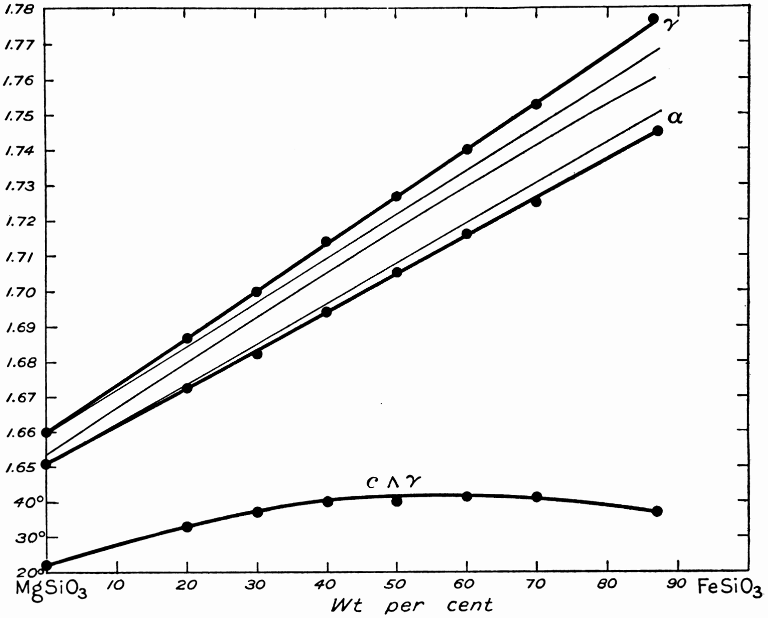

Fig. 26. *Heavy curves.* Refractive indices, γ and α, and extinction angles of monoclinic Mg-Fe pyroxenes. The curve for β is omitted because it lies very close to and nearly parallel to the curve for α. *Light curves.* Most probable values of the refractive indices, γ, β and α, of the orthorhombic Mg-Fe pyroxenes.

---

[24] Certain natural bronzites with obscure twin bands showing low extinction angles are discussed briefly on p. 169. It may be added that one of us (B) has noted that an obscure polysynthetic twinning, with low extinction angles of the bands, is prevalent in the olivine of ultrabasic rocks as well as in orthorhombic pyroxene.

If the composition is plotted in weight per cent the variation of the refractive indices, within the error of measurement, is linear. In Fig. 26 only γ and α are plotted; the curve for β would be practically parallel to that for α and very close to it. For comparison the figure shows curves of the three refractive indices of orthorhombic pyroxenes as light lines, the values used being those from the literature that appear to be the most reliable and significant determinations upon natural minerals. The much higher birefringence of the clino-pyroxenes except at the $MgSiO_3$ end is clearly brought out.

The optical properties of the Mg-Fe clino-pyroxenes are summarized in Table VI.

TABLE VI.

Optical Properties of Synthetic Mg-Fe Clino-pyroxenes.

Composition wt. per cent		Refractive indices		Extinction angle	Optic axial angle and orientation
$MgSiO_3$	$FeSiO_3$	γ	α	$c \wedge \gamma$	
100	0	1.660	1.651	22°	All have
80	20	1.687	1.673	33	a small +
70	30	1.700	1.682	37	optic axial
60	40	1.714	1.694	40	angle of
50	50	1.727	1.705	40	some 20°-25°
40	60	1.740	1.716	42	and plane
30	70	1.752	1.725	42	of optic axes
13	87*	1.777	1.743	36	⊥ 010

* This clino-pyroxene was prepared by inverting a natural ortho-pyroxene from Tunaberg, Sweden, which contains 42.23 per cent FeO and 3.88 per cent MnO.

Glasses.

Only a limited range of compositions in the system can be quenched to a glass. Examination of Fig. 27 shows clearly what range is covered. In that figure all the mixtures that were quenched to glass are plotted and the determined refractive indices are indicated by isofracts or curves of equal index, the numerical values being given in Table I. The area which embraces the determined points lies in a general way along the trough between the olivine field on the one hand and the silica (cristobalite-tridymite) fields on the other, a trough partly occupied by the pyroxene field (Figs. 5 and 6).

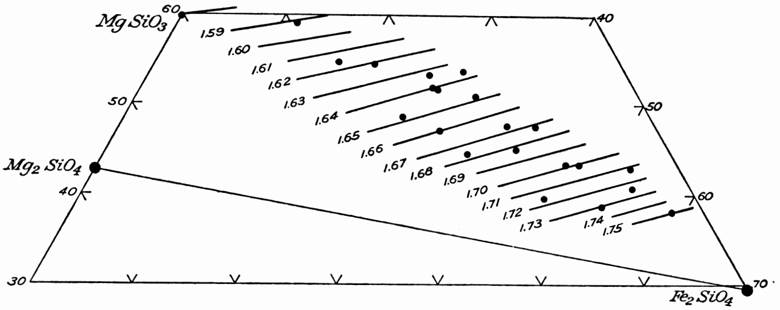

Fig. 27. Refractive indices of glasses.

BEARING OF THE RESULTS UPON PETROLOGIC PROBLEMS.

The pyroxenes and the olivines are among the most important of rock-forming minerals. The natural minerals, particularly the pyroxenes, are of more complex character than the simple members here studied, and especially are formed from more complex liquids than those of the present system. Nevertheless, some of the equilibrium relations here found are of general significance in rock problems and are a necessary step in the solution of the broader problem.

Pyroxenes and their Equilibrium Relations.

The monoclinic pyroxenes of the $MgSiO_3$-$FeSiO_3$ series are but little known to the petrologist, the clino-enstatite of meteorites being the most familiar representative among natural products. The controlling factor is no doubt the same as that determining the absence in nature of pseudo-wollastonite, carnegieite, and many other crystalline silicates familiar to laboratory workers. They are high-temperature forms and are represented by their low-temperature equivalents, usually because the natural solutions and melts crystallize only at low temperatures. When Mg-Fe metasilicate crystallizes from magmas it almost invariably assumes the orthorhombic form, stable at temperatures below 1140° at the magnesian end and below 955° at the other extreme. It is safe to conclude, therefore, that the crystallization of orthorhombic pyroxene took place below the temperatures mentioned, and since orthorhombic pyroxene is one of the earliest of minerals in those rocks in which it occurs, the indications of low-temperature crystallization of these rocks are clear. Moreover, the change of volume involved in the inversion is so small (as suggested by the near identity of mean refractive index) that the effect of pressure will be negligible. The conclusion reached as to the maximum temperature of crystallization of orthorhombic pyroxene will hold for any depth.

There is already a great body of evidence pointing to the crystallization of the more complex rocks at moderate temperatures, so the facts just pointed out represent merely further confirmation of opinions widely held. There are, however, rocks of especially simple constitution whose conditions of formation are a matter of debate. Among these are rocks made up almost exclusively of orthorhombic pyroxene. Some petrologists favor the opinion that these rocks crystallized directly from a melt of their own composition. The present study shows conclusively that such crystallization would take place at temperatures far above those at which orthorhombic pyroxenes would form. It seems clear, too, that the ortho-pyroxenes of these rocks were orthorhombic from the beginning and are not the product of inversion from the high-temperature monoclinic form. In a sufficient number of such rocks ortho-pyroxene exhibits the outward form appropriate to orthorhombic symmetry.

The alternative then naturally suggests itself that the rocks under consideration did indeed crystallize from magmas of approximately their present composition but containing volatile constituents that lowered the temperature of crystallization and were lost during that process. But when we consider the fact that a temperature-lowering of some 300° would probably be required (the interval between the liquidus and the inversion curve is upwards of 400° in the pure minerals, see Fig. 8), we may reasonably doubt whether the necessary quantity of volatiles could have been present and yet leave no evidence of their presence in the formation of hydrous phases such as amphibole, which are often entirely lacking.

The alternative to which we seem to be driven is the concept that most rocks made up of orthorhombic pyroxene were formed as the result of local accumulation of crystals of one kind from a magma of complex constitution, crystallizing at the low temperature appropriate to such constitution.

The orthorhombic pyroxenes of the rocks just discussed are always highly magnesian, a fact in keeping with their presumed origin as accumulated early crystals. Iron-rich ortho-pyroxenes have a totally different origin. They occur in cavities of lavas where they are formed by solutions or vapors, or again in such rocks as eulysite where the intervention of mineralizing solutions is highly probable. As compared with truly magmatic minerals they belong to a relatively low temperature phase of activity and it is not surprising that they assume the orthorhombic form.

Although one can reach the definite conclusion that orthorhombic pyroxene did not form at high temperature, the converse does not necessarily follow. It is not safe to assume that the monoclinic modification of the Mg-Fe pyroxenes must form only at high temperatures. It is a common observation that crystalline phases stable only at high temperatures may form metastably at low temperatures especially if rapidly formed, and in this respect clino-pyroxenes of the present series are no exception. Among rock minerals there are no clino-pyroxenes belonging strictly to this series, but the pyroxenes low in CaO known as pigeonite approach it rather closely.[25] An interesting example of these is the "uniaxial augite" from Mull described by Hallimond.[26] Minor constituents aside, its composition may be expressed approximately as $MgSiO_3$ 35 per cent, $FeSiO_3$ 56 per cent, $CaSiO_3$ 9 per cent by weight. In optical properties it shows a close approach to a pyroxene of the pure Mg-Fe clino-series having $MgSiO_3$ 40 per cent, $FeSiO_3$ 60 per cent. There can be little doubt that the stable condition of the substance of this uniaxial augite at low temperatures would be an orthorhombic pyroxene with a small admixture of lime-rich monoclinic pyroxene, and the suggestion is that these crystals formed at a high temperature. Unfortunately, this cannot be regarded as established, for, as we have seen in the foregoing, they could presumably form metastably at a temperature below the range of their stable existence. The inversion temperature of their closest relative in the pure $MgSiO_3$-$FeSiO_3$ series is about 1050°. Their inversion or unmixing temperature would be somewhat lower, but even so it is not probable that these crystals formed above that temperature.

The same remarks may be made with reasonable assurance of most pigeonites. They are probably formed metastably at

---

[25] The clino-enstatite crystals with rims of enstatite described by Holmes and Harwood should here be noted. They are in the normal relation to be expected with falling temperature. Quart. Jour. Geol. Soc. London, **88**, 404, 1932.

[26] Hallimond, A. F.: Min. Mag., **17**, 97-99, 1914.

temperatures below their stability range. In those examples where they occur as phenocrysts it is possible that they were stable crystals, but in the great majority of occurrences as part of the general fabric of basaltic rocks they were probably formed metastably during rapid crystallization. The stable arrangement resulting from very slow, equilibrium crystallization, at the same temperature, would be a mixture of orthorhombic pyroxene and highly calcic clino-pyroxene.

These conclusions, strongly indicated by experimental results, are supported by the actual relations in some rocks. Thus Tsuboi finds that the phenocrysts of Japanese andesitic and basaltic rocks, representing slow intratelluric crystallization, are of "both monoclinic and rhombic pyroxenes."[27] On the other hand, the groundmass pyroxenes, representing rapid crystallization, "are, with rare exceptions . . ., all pigeonitic"[28] but in the rare cases where rhombic pyroxenes are found along with monoclinic in the groundmass, the groundmass tends to be high in crystallinity.[29] In other words, if the ordinarily rapid crystallization of the groundmass is sufficiently slowed down, the stable configuration, consisting of the two different types of pyroxene, is reached as definitely there as it is in the porphyritic elements.[30]

Olivines and Olivine-rich Rocks.

Among the most interesting of rocks are those consisting entirely or almost entirely of a single mineral. Their very simplicity presents a problem of the utmost difficulty. Prominent among these monomineralic rocks are the ultrabasic types

---

[27] Tsuboi, S.: Jap. Jour. Geol. Geog., X, p. 68, 1932.

[28] Op. cit., p. 78.

[29] Op. cit., pp. 71-2.

[30] Although the above explanation of pigeonites as a metastable phenomenon seems acceptable for some rocks it probably does not apply generally. The interesting "pseudo-hypersthenes," recently described from North China, and consisting of a mixture of olivine and pigeonite, pseudomorphous after hypersthene (T. Tomita, J. Shanghai Science Inst. I, 1933, 3) indicate that pigeonite may sometimes be formed at lower temperatures than associated orthorhombic pyroxene, unless it should happen that we are, in this instance, dealing with a change effected by rising temperature, a possibility that the formation of olivine suggests. But this possibility seems to be definitely precluded in the Whin Sill type of quartz dolerite to which our attention has been called in this connection by Dr. Frederick Walker. These dolerites may have all three pyroxenes, orthorhombic, pigeonitic, and lime-rich, in the one rock, separated in the order given. Plainly it is necessary to investigate pyroxene compositions of more complex character before a satisfactory general explanation of pigeonites is forthcoming.

made up entirely of pyroxene or of olivine. We have already discussed the origin of rock masses consisting of orthorhombic pyroxene and concluded that the evidence appears to favor the concept that they were not formed by simple crystallization of a melt of their own composition but rather by accumulation of crystals from a complex magma. The same concept has been advanced elsewhere as a probable mode of origin of ultrabasic rocks in general, olivine rocks, including dunites, being especially emphasized.[31] It has met with rather wide acceptance, but some adherents believe that, as olivine crystals accumulate (usually by sinking) they are resorbed or remelted, that thus liquids very rich in the materials of the accumulating crystals are produced, and that from such liquids monomineralic and closely related rocks are formed by simple crystallization.

Johann Vogt was a leading exponent of this view, and with the courage of his convictions he accepted the high temperatures necessary to the existence of dunitic magma, in so far as the temperatures were then known. He states: "The temperature of the beginning of crystallization must have been . . . for the dunites at least 1500, occasionally even 1550-1600°."[32] Vogt's temperatures were the best estimates then available and were based on an assumed form of the equilibrium diagram of the system, Mg_2SiO_4-Fe_2SiO_4, in which the liquidus fell off precipitately from the known value 1890° at Mg_2SiO_4, with small additions of Fe_2SiO_4. Fig. 7 shows how far this is from the truth. At a composition where Vogt supposed that the melting temperature would be about 1500° (20 per cent Fe_2SiO_4) it is in reality well above 1800°. Many petrologists found even Vogt's temperatures unacceptable. Thus Harker expressed the opinion that no support is to be found for belief in such temperatures at the time of intrusion of dunites, a remark that would apply with greater emphasis to the temperatures now known to be necessary.

It is sometimes assumed that the olivine rocks contained a large proportion of volatile fluxes now lost. Some of them, such as mica peridotites, may very well have done so, but for many examples, including typical dunite, the assumption is wholly gratuitous. Evidence for the abundant presence of volatile constituents is entirely lacking.

---

[31] Bowen, N. L.: This Journal, **14**, 89-108, 1927.

[32] Vogt, J. H. L.: Vidensk. Selsk. Skr. I, Mat. Naturw. Kl., 1924, No. 15, p. 97.

We appear to be reduced to the conclusion that dunites are formed by accumulation of crystals, with perhaps some special mode of intrusion of a crystalline mass for those bodies that seem to be independent intrusives. But discussion of such matters is beyond the scope of this paper. We wish merely to emphasize the difficulties in the way of acceptance of dunitic magma unless there is evidence of the very high temperatures that this investigation has shown to be necessary to its existence, or of the abundant presence of volatile fluxes.

Liquid Peridotite Layer in the Earth.

While we are on the subject of dunitic magma it is perhaps desirable to remark upon the problem of a liquid layer of peridotite (related to dunite) within the earth. In this connection the probable density of the liquid olivine and the effect of pressure upon the melting temperature become important. While we have no intention of discussing the merits of the general theory, our data do permit an estimate of the effect of pressure upon the melting point of olivines which may prove of value in the absence of any better information.

The effect of pressure upon the melting point of any substance depends entirely upon the volume change and the heat effect attending fusion. By applying the theory of ideal solutions to the determined equilibrium diagram of the olivines, values are to be obtained for latent heats of melting. By applying the law of Gladstone and Dale connecting the refractive index and the density of silicates, we may, with the aid of some extrapolation, obtain the volume change of olivines on melting. Objections are to be raised to the precise validity of both theories, but the results of carrying through the reasoning are not without some orienting value.

Latent Heat of Fusion of Olivines.

The olivine diagram is of the same form as the plagioclase diagram to which the theory of ideal solutions has been applied. The method of derivation of the equation is not altogether acceptable in these times but the actual equations reached and used are valid, assuming ideality. It is of interest, in any case, to apply them to the experimental results obtained for the olivines. The equations connecting the concentrations, x and x_1, upon the liquidus and solidus, respectively, at any temperature T with the molal latent heats L_1

and L_2 and the absolute melting points T_1 and T_2 of the two components are as follows, R being the gas constant,

$$\ln \frac{1-x}{1-x_1} = \frac{L_1}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)$$

$$\ln \frac{x}{x_1} = \frac{L_2}{R}\left(\frac{1}{T_2} - \frac{1}{T}\right).^{33}$$

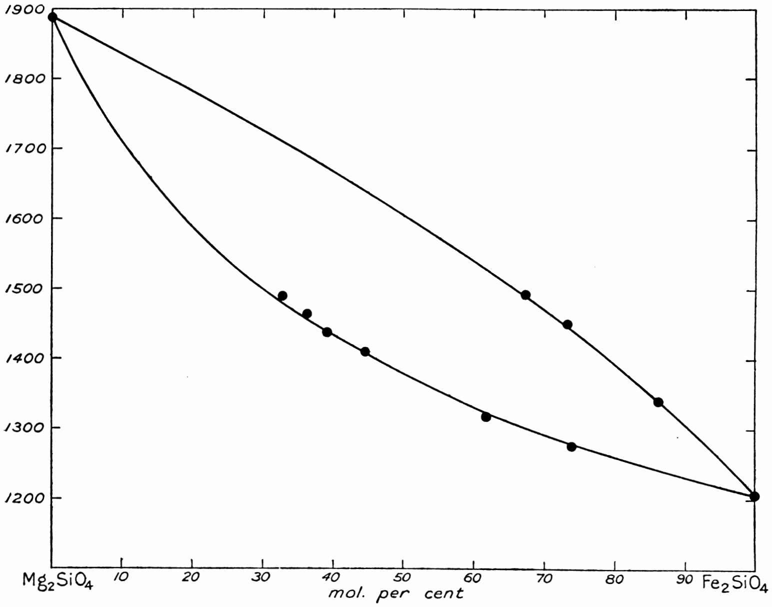

Fig. 28. Calculated solidus and liquidus curves for the system, forsterite-fayalite, using 14000 cal. as molal latent heat of each. Solid circles indicate points determined experimentally.

Preliminary calculations from determined points indicated values approaching 14,000 cal for the molal latent heat of both fayalite and forsterite. The process was then reversed; complete curves were calculated and plotted using the value 14,000 cal for the molal latent heats, and the determined points were then put on the plot. The result is shown in Fig. 28, the curves being the calculated curves and the solid circles the determined points. The deviation of the points from the curves is within the experimental error of determination of the points, the greatest deviation being shown by

---

[33] Bowen, N. L.: This Journal, **35**, 589, 1913.

solidus points which are also those that carry greatest possible error of measurement. The high-temperature portions of the curves lack determined points, except the melting point of forsterite, but with these limitations, and in so far as the theory applied is valid, we may take it that the results indicate molal latent heats of melting of forsterite and fayalite sensibly equal and of a value close to 14,000 cal. This gives in round numbers 69 cal per gram and 100 cal per gram, respectively, for fayalite and forsterite.

Volume Change of Olivines upon Melting.

We have made no determinations of the densities of olivines because the materials as prepared do not lend themselves to such determinations, but we have measured their refractive indices. No olivine glasses are available for the measurement of refractive indices because we found it impossible to prepare such glasses, but we have determined refractive indices of many glasses in the system. From these it is possible to obtain indications of the refractive indices of olivine glasses by extrapolation, never wholly satisfactory, but the best means available in this instance. By applying the law of Gladstone and Dale which indicates that $\frac{n - 1}{d}$ = constant whether the substance is glass or crystals, we obtain, from the ratio of $n - 1$ for the crystals to $n - 1$ for the glass, the ratio of the density of glass to the density of crystals. The refractive indices of olivine glasses have been obtained by extrapolating the isofracts of Fig. 27 until they intersect the Mg_2SiO_4-Fe_2SiO_4 join.

In Table VII the results of these operations are given. It is there seen that the change of volume of olivines upon melt-

TABLE VII.

Change of Volume of Olivines upon Melting as Indicated by Change of Refractive Index.

Composition weight Mg_2SiO_4	 Fe_2SiO_4	Refractive index of glass (Extrap.) ngl	Mean refractive index of crystals nxl	$\frac{(nxl-1)}{(ngl-1)} = \frac{vgl}{vxl}$
100	0	1.634	1.652	1.028
75	25	1.667	1.687	1.029
50	50	1.714	1.734	1.027
40	60	1.732	1.754	1.030

ing suggested by change of refractive index measured at room temperature is about 3 per cent. The method applies only over to about 60 per cent Fe_2SiO_4 because, for the mixtures richer in iron, there are not enough points to determine the direction of the isofracts. Within the determined range there is no adequate evidence of systematic variation. Even if the isofracts, sensibly straight in the determined portion, acquired a curvature, in the extrapolated portion, as great as that exhibited in the $CaO\text{-}FeO\text{-}SiO_2$ system,[34] the indicated volume change would be only about 4 per cent.

Effect of Pressure upon the Melting Point of Olivines.

With the small change of volume upon melting suggested by these considerations the effect of pressure upon the melting point of olivine will be correspondingly small. We may calculate the effect of pressure from the volume change and the heat effect with the aid of the Clausius-Clapeyron equation

$$\frac{\mathrm{d}T}{\mathrm{d}p} = \frac{\Delta V}{\Delta H} T.$$

The density of forsterite is 3.223[35] and $\Delta V = 0.0093$ cm^3 per gram, and the heat effect ΔH is 100 cal per gram, whence $\frac{\mathrm{d}T}{\mathrm{d}p} = 0.0047$ degrees per atmosphere. A pressure of 1000 atmospheres should therefore raise the melting point of forsterite 4.7°.

Our determinations enable us to estimate the volume change of olivines, upon melting, only about half way over to fayalite, where it still appears to be only 3 per cent. If the same value applied to fayalite, a pressure of 1,000 atmospheres, would raise the melting point only about 3.5°, whereas Goranson[36] has recently found by direct measurement a raising of approximately twice that much. A rapid increase (doubling) of the volume change toward the fayalite end is suggested or, not impossibly, our estimate for the magnesium members may be off 100 per cent, based as it is upon figures obtained by such indirect methods. In any case the volume change of olivines upon melting is considerably less than that occurring with

---

[34] Bowen, N. L., Schairer, J. F., and Posnjak, E.: Op. cit., Fig. 31, p. 264.

[35] Aurousseau, M., and Merwin, H. E.: Am. Min., **13**, 563, 1928.

[36] Personal communication.

most rock-forming silicates and is probably very small in the more magnesian members which have the greater importance to the petrologist.

Fractional Crystallization.

The fractional crystallization of liquids of the system, MgO-FeO-SiO_2, is remarkable in the possible scope of its results, yet at the same time of rather simple character. In these respects it is not unlike the same process in liquids of the plagioclase system, anorthite-albite. Just as in this latter system the composition albite is the goal towards which all liquids strive during fractional crystallization, so in the present system all liquids strive to reach the composition of the point *M* (Fig. 22).[37] In detail the process is, of course, much more complicated than in the simple binary system of the plagioclases.

Some liquids of the system begin to crystallize with separation of highly magnesian olivine and reach the boundary curve *KL* at a point between *K* and *O* (again Fig. 22). All of these except those in the triangle *KJO* are liquids having a deficiency of silica below the metasilicate ratio (which we shall refer to as *undersilicated*) but upon encountering the curve *KO* they fail to follow it, as they would in non-fractional crystallization. Instead, they precipitate pyroxene only and cross the pyroxene field, acquiring a notable excess of silica over the metasilicate ratio (oversilicated) and reaching the boundary curve *FGRL* which they follow with separation of pyroxene and free silica (cristobalite or tridymite). If fractionation is limited (reaction between liquid and crystals only moderately restricted) the liquid may become completely exhausted when its composition is represented by some point between *G* and *R*. The final liquid is still oversilicated.

On the other hand, if the fractionation is stronger (reaction between liquid and crystals more restricted), some liquid may remain and continue to change composition along *RL*, thus becoming undersilicated once again. In the ideal case of perfect fractionation (complete lack of reaction between liquid and crystals) the liquid would continue past *L* and follow *LM*, olivine and tridymite now separating, until a final infinitesimal quantity of the liquid reached the composition *M*. The crys-

---

[37] We omit, as being of no importance in the present connection, all liquids of lower silica content than the orthosilicate ratio. It is to be noted also that pure olivine liquids fractionate not towards *M* but towards pure fayalite.

talline products of this last example would range all the way from highly magnesian olivine as the earliest crystals, through highly magnesian pyroxene accompanied by silica, then more ferriferous pyroxene accompanied by silica, to highly ferriferous olivine again accompanied by silica.

Most oversilicated liquids of the system will encounter and follow the curve *FL* during their fractional crystallization and may eventually proceed along *LM*, if fractionation is adequate, in exactly the same manner as the liquids just discussed. Some few oversilicated liquids first encounter the boundary curve *LM* and then proceed along it.

Those undersilicated liquids that reach the boundary curve *KOL* at points between *O* and *b* do not immediately follow that curve. They pass into the pyroxene field with separation of pyroxene but, never becoming oversilicated, follow a curved course that brings them back again to the boundary curve *KOL* which they then follow towards *L*. They attain *L* and pass on towards *M* if conditions permit an adequate degree of fractionation.

Those undersilicated liquids that reach the boundary curve *KOL* between *b* and *L* follow the curve to *L* during their fractional crystallization and may pass on towards *M* if fractionation is adequate, and, of course, some undersilicated liquids encounter *LM* directly.

The perfect equilibrium (non-fractional) type of crystallization discussed on earlier pages may be a very complex process but, when it is completed, the crystalline product is of simple constitution. At the other extreme the type of crystallization showing maximum fractionation is, in general, not so complex a process; but it is extended through a much wider range of temperatures and yields a crystalline product with a greater number of phases and a wide range of composition of the variable phases (solid solutions). These results grow out of the prevalence of incongruent melting and solid solution in the system. It is this principle of flexibility of crystallization introduced by the phenomena just mentioned that renders the course of crystallization and the products of it responsive to the conditions attending crystallization. The importance of this principle has been pointed out elsewhere,[38] but no apology is here offered for emphasizing it once again especially in connection with experimental results upon such important rock-forming minerals as pyroxenes and olivines.

---

[38] Bowen, N. L.: The reaction principle in petrogenesis, J. Geol., **30**, 177-198, 1922.

The fact that the pyroxene series of solid solutions of this system shows the one type of incongruency at one end of the series and the opposite type at the other end is a matter of much interest. The incongruent melting of clino-enstatite with separation of olivine and the consequent throwing of excess silica into the liquid has been made a point of great importance in the theory of the derivation of salic magmas from basaltic magma by fractional crystallization. To some it may seem that, since the addition of 20 per cent of $FeSiO_3$ to clino-enstatite completely neutralizes this tendency, the foundation of the theory is greatly weakened, and this would be true if the whole story were as just stated. Rather is it that the discovery of the incongruent melting of $MgSiO_3$, and its consequences, pointed to an explanation, by appeal to analogy, of the long observed fact that the olivines of certain rocks have suffered resorption, with the development of reaction rims of pyroxenes about them, and that in many basaltic rocks in which this is observed, a highly siliceous, interstitial crystallization-residuum is found. Other explanations of these phenomena had been and still are offered, notable among which is that which appeals to the effects of volatile components, but no one has been able to offer the slightest suggestion of evidence that volatile components could bring about such a result, whereas appeal to analogy with the phenomena observed in experimental studies furnishes something definite and tangible as a basis for our reasoning. Just which compositions of pyroxene and olivine will show the relation necessary to give a residual liquid enriched in silica we cannot know until experimental studies have covered a wider range of compositions. It has been ascertained that the important pyroxene, pure diopside, does not bear the necessary relation to olivine but, on the other hand, a wide range of pigeonite-like pyroxenes between diopside and clino-enstatite do have it.[39] The present investigation shows that those pyroxenes of the $MgSiO_3$-$FeSiO_3$ series containing more than 20 per cent $FeSiO_3$ fail to show the required relation. But even when these studies have been carried forward to include still more complex pyroxenes, it will still be necessary to ascertain the effects of addition of other phases such as feldspar, for these can exert specific effects upon the relation in question. The influence of anorthite upon the melting-relation of clino-enstatite has already been examined[40] and found to more than

---

[39] Bowen, N. L.: This Journal, **38**, 207-264, 1914.

[40] Andersen, O.: This Journal, **39**, 407-454, 1915.

treble the amount of "excess" olivine that can separate. All of these investigations are to be regarded as a concerted effort to lessen the gap between investigated systems and natural magmas, in order that the facts gleaned from the investigations may be applied with ever-increasing confidence to the interpretation of magmatic phenomena. In the meantime, we must make applications as best we may, realizing that some of the conclusions will inevitably require modification with increased knowledge.

An example of such a situation is furnished by our present results. The fact that in liquids of the system, MgO-SiO_2, forsterite, if any forms at all, will necessarily separate before clino-enstatite, has been used to explain the observation that ordinarily in rocks olivine, even when present in very small amount, has evidently separated at a very early stage and especially before pyroxene. This relation may be expected to hold the more rigidly the more our natural olivine and pyroxene approach a highly magnesian composition, but, as the natural olivine and pyroxene depart from this composition, the relation between them will suffer concurrent modification. The present results show that a different relation obtains if the olivine and pyroxene have a high iron content. Thus from all liquids in the area *ORL* of Fig. 22 pyroxene separates first and is followed by olivine, which is then comparatively rich in iron. It is not surprising, therefore, to find that some rocks are exceptions to the general rule in that they show separation of olivine after pyroxene. Thus Backlund and Malmquist describe Greenland basalts that have this character and, appropriately, the olivine contains iron in amounts far beyond that ordinarily present in basaltic olivines.[41]

These exceptions do not render necessary any modification of the general conclusion that the olivines of basalts ordinarily bear a reaction relation to pyroxene and that, in consequence of this, oversilicated late differentiates can be formed. Nevertheless, they do call attention to the fact that this relation does not universally hold and that for certain iron-rich basalts such late differentiates are not to be expected, but rather undersilicated, alkalic types. It is not probable, however, that distinct parental magmas are absolutely essential to the development of these contrasted late differentiates. As has been suggested elsewhere, a certain amount of flexibility in this respect

---

[41] Backlund, Helge, and Malmquist, D.: Meddelelser om Gronland, Bd. 87, Nr. 5, p. 45, 1932.

may be introduced by variation in the rate of cooling of one and the same initial magma.[42] The principles involved are illustrated once again in the present system, with residual liquids alternatively undersilicated or oversilicated, depending upon the degree of fractionation in crystallization.

In this connection attention is to be called to the small change of volume of olivine upon melting, as compared with that of pyroxene, because it indicates that at high pressures the pyroxene field will be extended at the expense of the olivine field and the incongruent character of the melting of pyroxene will disappear. How important this may be in a natural magma it is impossible to predict. We have the tendency of $FeSiO_3$ and of high pressure to suppress incongruency and on the other hand the tendency of the anorthite molecule to enhance it, and the state of balance between these and other factors now unknown is not determined by any experimental investigation. Natural rocks do, however, seem to indicate the persistence of the reaction relation of olivine in some magmas at all depths that come under our notice.

Olivines and Pyroxenes of Metamorphic Rocks.

In an igneous rock there is an order of separation of its constituent minerals, and between the period of separation of one mineral and another there is a change of composition of the liquid. At the time of its separation each of two minerals may have been in equilibrium with the liquid as it then existed but frequently they may not be in equilibrium with each other. Thus we are accustomed to find that in igneous rocks containing olivine and pyroxene the olivine is ordinarily more magnesian than the pyroxene. Yet the olivine in equilibrium with a pyroxene, if they approach the composition of those phases in the present system, should be less magnesian than that pyroxene, as shown graphically in the isothermal figures 9-18. Olivine and hypersthene formed simultaneously in a rock, by recrystallization during a metamorphic episode, should be such that the olivine contains less of the forsterite molecule than the hypersthene does of the enstatite molecule. There are probably not enough observations to permit a statement as to how generally this expectation is borne out in such rocks.

---

[42] Bowen, N. L.: The Evolution of the Igneous Rocks. Princeton, 1928, pp. 236-240.

The Quartz Basalts.

The type of incongruent melting, opposite to that with which we have heretofore been concerned, probably has no petrologic importance. This melting with separation of silica, or its converse early separation of silica from the liquid, occurs only with pyroxene very rich in $FeSiO_3$. Such pyroxenes do not appear in rocks formed directly from magmas but are rather the product of low-temperature, metasomatic processes, and the question of their melting relations does not enter.

Those liquids of the system from which olivine and free silica can separate side by side in equilibrium with each other are of interest in connection with the problem of quartz basalts. In these rocks quartz and olivine were present together in a largely liquid magma and the quartz reacted with the liquid, giving pyroxene rims about remnants of the quartz grains. Some investigators have regarded the quartz grains as representing material acquired from extraneous sources.[43] On the other hand, some are of the opinion that the quartz is, like the olivine, a product of early crystallization from the basaltic liquid.[44]

Although free silica and olivine can occur together in equilibrium with liquid and therefore with each other in the present system, this is true only of olivine with 68 or more per cent fayalite. Even this olivine is in equilibrium with free silica at the temperature 1305°. At lower temperatures it reacts with silica and only a still more highly ferriferous variety can then persist in equilibrium with silica. We have determined optically the olivine in a typical specimen of quartz basalt from Rio Grande Canyon, New Mexico, and have found it to have somewhat less than 25 per cent Fe_2SiO_4.[45] There is no support in the present studies for the belief that such an olivine can form in equilibrium with free silica. A word should be said about the possibility that, with increase of pressure, the narrow, wedge-shaped field of the pyroxenes (Fig. 5) would become still narrower and finally disappear, thus

---

[43] Harker, A.: Natural History of Igneous Rocks, 1909, p. 355.
Finch, R. H., and Anderson, C. A.: Univ. Cal. Bull. Geol., **19**, 245-273, 1930.

[44] Iddings, J. P.: This Journal, **36**, 220, 1888.
Diller, J. S.: U. S. G. S., Bull. 79, 24-30, 1891.

[45] The particular specimen was U. S. G. S. Petrographic Reference Collection No. 548. Finch and Anderson (Op. cit., p. 261) found olivine of nearly the same composition in quartz basalts from Lassen Peak.

bringing into general contact the fields of olivine and of silica. The possibility cannot be categorically denied, perhaps, but indications are strongly against it. A tendency in this direction could occur only if the passing into solution of pyroxene were attended by a much smaller increase of volume than that occurring when olivine and silica passed into solution. Upon this question we may take the changes of volume of the phases upon melting as a reasonably reliable guide. Pyroxenes do show a somewhat smaller change of volume than does silica (as quartz) but, on the other hand, they show, as we have seen, a much larger change than olivines do. It is probable, then, that the pyroxene field of the present system would maintain its width at higher pressures and that the conclusion stated above requires no qualification for such conditions. This is the nearest indication, now obtainable from experiment, as to the possible suppression of the pyroxene field in natural magmas at high pressures.

TECHNOLOGIC APPLICATIONS.

The contrasted effects of CaO and of MgO upon the melting temperatures of FeO-SiO_2 mixtures are readily brought out by comparison of the two ternary diagrams CaO-FeO-SiO_2[46] and MgO-FeO-SiO_2. The initial effect of the addition of CaO to ferrous silicates is to lower the melting temperatures. The lowest melting mixture of the system (1093°) contains 17 per cent CaO and a wide range of compositions in the neighborhood of this minimum have melting temperatures below 1150°. Such compositions are thus inherently of the nature of slag and it is not surprising that slags of this character are used in non-ferrous metallurgy and, to some extent, in the "acid" processes of iron metallurgy.

On the other hand, from the very beginning, addition of MgO raises the melting temperatures of ferrous silicates, the fundamental cause being the prevalence of solid solution. No mixture with as much as 17 per cent MgO melts below 1400°. For this reason MgO is not ordinarily a desirable addition to such slags. But for the same reason MgO and Mg-rich materials are highly resistant to the fluxing action of the FeO and ferrous silicates contained in slags.[47] Burned mag-

---

[46] Bowen, N. L., Schairer, J. F., and Posnjak, E.: This Journal, **26**, p. 205, Fig. 6, 1933.

[47] Fisk, H. G., and McCaughey, W. J.: Bull. 70, Engineer. Experiment Station, Ohio State Univ., 1932.

nesite or periclase in the hearth of an open-hearth steel furnace can absorb into itself large quantities of FeO from the metal bath, forming a solid solution with it that does not begin to melt except at a very high temperature (see Fig. 3). Likewise Mg_2SiO_4, or an olivine close to it in composition, formed, say, by the action of a silicate slag on a magnesite refractory or actually used as refractory blocks itself, can absorb as much as 25 per cent Fe_2SiO_4 and yet not suffer beginning of melting at 1600°. Burned lime in the same situation would be notably fluxed, some liquid being formed in the presence of the ferrous silicates of the slags at decidedly low temperatures. It is to be noted, however, that this does not apply with equal force to the CaO present in burned dolomite. The Ca.Fe silicates have lower temperatures of beginning of melting than the Ca.(Mg,Fe) silicates and the periclase of the burned dolomite will thus in some measure prevent too ready fluxing of CaO while, at the same time, introducing its own inherent resistance to fluxing by iron silicates.

SUMMARY.

In view of the great importance of ferromagnesian silicates as rock-forming minerals a study of equilibrium in the system, MgO-FeO-SiO_2, has been carried out.

No ternary compounds are formed. The system is dominated by three series of solid solutions, the oxide series, MgO-FeO, which is complete, the orthosilicate or olivine series, Mg_2SiO_4-Fe_2SiO_4, likewise complete, and the metasilicate or pyroxene series, $MgSiO_3$-$FeSiO_3$, which is only partial, since $FeSiO_3$ does not exist as such, although solid solutions with nearly 90 per cent of that molecule are formed. The fields of these three mix-crystal series, together with the fields of silica as cristobalite and tridymite, occupy the whole liquidus surface of the triangle (see Fig. 5).

The broader temperature relations are comparatively simple. The magnesian end members of the solid solution series are invariably of higher melting temperature, with the result that the low liquidus temperatures all lie on the FeO-SiO_2 side of the triangle (see Fig. 6). More specifically, the oxide series is of Type I (Roozeboom), the olivine series, of the same type, has a melting temperature of 1890° at the Mg_2SiO_4 end, and of 1205° at the Fe_2SiO_4 end (see Fig. 7). The pyroxene series is much more complicated, by reason of the fact that

at the magnesian end incongruent melting occurs, with separation of olivine, while at the other extreme incongruent melting with separation of silica prevails, and in connection with this latter phenomenon, the pyroxene field wedges out entirely at 1305°, below which temperature olivine and tridymite fields are in juxtaposition (see Fig. 6).

The relations of the metasilicates are further complicated by the fact that they form two mix-crystal series, the monoclinic stable at high temperatures, and the orthorhombic stable at low temperatures. The inversion temperature falls from 1140° at the pure magnesian end-member, to 955° at the iron-rich extreme. A section along the metasilicate join, even although it is not a binary diagram, brings out clearly these characters together with the variant incongruent melting mentioned above (see Fig. 8).

On account of the prevalence of solid solutions and of incongruent melting the courses of crystallization are of particular interest, especially in connection with the potentialities of fractional crystallization. These are discussed in detail, with application to natural magmas.

The simple character of the olivine diagram renders it possible to calculate, under certain assumptions, the latent heats of melting of olivines. The value indicated is 14,000 cal per mol for both forsterite and fayalite, from which 100 cal per gram and 69 cal per gram respectively are obtained. An estimate based on refractive-index measurements has been made of the change of volume of the more magnesian olivines upon melting, the value 3 per cent being indicated, and with these two factors as a basis the change of melting-point of forsterite with pressure is calculated as 4.7° per 1000 atm.

The optical properties of the several phases have been determined and are presented in tabular and graphic forms (see Tables IV-VI and Figs. 24-27).

Brief mention is made of the application of the results to slags and refractories.

Geophysical Laboratory,
Carnegie Institution of Washington.
October, 1934.