THE SYSTEM DIOPSIDE—FORSTERITE—ANORTHITE

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ABSTRACT. The system diopside—forsterite—anorthite is an example of a system containing a pyroxene, an olivine, and a feldspar in which virtually no solid solution or reaction relation among the phases exists. This system, however, may be considered as one face of a tetrahedron representing the system diopside—forsterite—anorthite—silica which is noteworthy for crystal-liquid reaction phenomena as liquids crystallize under equilibrium conditions. Phase equilibrium data are presented and their bearing on the crystallization of spinel from basaltic liquids and on the formation of coronite is discussed.

INTRODUCTION

THE minerals diopside ($CaMgSi_2O_6$), forsterite (Mg_2SiO_4), and anorthite ($CaAl_2Si_2O_8$) are representatives of three mineral groups of common occurrence, the pyroxenes, olivines, and feldspars. These three groups play an important role in the formation of igneous rocks,[1] indeed are quantitatively the major silicate structures composing the earth's crust. Olivines are constructed of isolated SiO_4 tetrahedra bound together by divalent ions of medium size, usually Mg^{2+} and Fe^{2+}; pyroxenes are composed of chains of linked SiO_4 tetrahedra united by medium or moderately large cations such as Mg^{2+}, Fe^{2+}, and Ca^{2+}; while the feldspars are characterized by a three-dimensional linkage of SiO_4 and AlO_4 tetrahedra into which network fit the large cations Ca^{2+}, Na^{+}, K^{+}, and others of similar size and charge. Owing to the fundamental difference in type of structure among the three groups, solid solution does not occur between any two of olivines, pyroxenes, and feldspars, but extensive solid solution exists within each group.

It was primarily to learn more of the phase relationships existing among these silicate types that the system diopside—forsterite—anorthite was investigated. But this system is also part of a larger project, an investigation of phase equilibria in the quaternary system $CaO—MgO—Al_2O_3—SiO_2$. This quaternary system is sketched in figure 1 as a tetrahedron having as apices the four components, CaO, MgO, Al_2O_3, and SiO_2. The four faces of the tetrahedron are ternary systems, and other ternary or partly ternary systems exist within the tetrahedron where certain combinations of three compounds are considered.

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[1] For a recent summary discussion of their role, see Osborn (1950).

The system diopside—forsterite—anorthite (triangle A-D-Fo, fig. 1) is one such combination of three compounds which as a first approximation may be treated as a ternary system. Neighboring systems which have been previously studied are the triangular joins: anorthite-forsterite-silica (Andersen, 1915), $CaSiO_3$-diopside-anorthite (Osborn, 1942), pseudowollastonite-akermanite-gehlenite (Osborn and Schairer, 1941), and diopside-anorthite-silica.[2] Owing to the existence of this group of interior triangular joins which are ternary or partly ternary systems, interior tetrahedra exist which for most purposes can be treated as quaternary systems. It can be seen in figure 1 that two such tetrahedra are present having as a common face the system diopside—anorthite—silica. With this investigation of the system diopside—forsterite—anorthite, phase equilibrium data have been obtained for all seven of the faces of the two interior tetrahedra. It is therefore possible to estimate phase relations within the tetrahedra with sufficient accuracy for many purposes. In the left tetrahedron (W-D-A-SiO_2, fig. 1), for example, two quaternary invariant points must exist at temperatures of approximately 1135° and 1150°C. In the right tetrahedron (D-A-Fo-SiO_2) no liquidus invariant points are present as three univariant lines pass continuously through the tetrahedron, one passing through a maximum and the others through a minimum temperature.

METHOD OF INVESTIGATION

In this investigation the method of quenching was used which has been described in many reports from the Geophysical Laboratory (for example, Osborn and Schairer, 1941, p. 716). Homogeneous glasses were prepared from the pure ingredients $CaCO_3$, MgO, Al_2O_3, and SiO_2. The crushed glass was completely crystallized by holding it for a minimum of one day at 1000°C. A charge of about 15 mg. of the powdered crystalline material was enclosed in a platinum envelope, held at a desired temperature for a time sufficient to attain a close approach to equilibrium among the phases, and quenched in mercury. Phases present in the quenched product were identified by means of a petrographic microscope. The platinum-platinum 90 rhodium 10 thermocouples were frequently calibrated at standard melting

[2] Approximate relations in this system are sketched in figure 7 after Greig (1949).

points defined as follows: Au, 1062.6°; $CaMgSi_2O_6$, 1391.5°; and $CaSiO_3$, 1544°.

LIMITING SYSTEMS

The system diopside—forsterite—anorthite is bounded by the three systems, diopside—forsterite, forsterite—anorthite, and diopside—anorthite, all of which have been previously investigated. The equilibrium diagram of the first of these, after Bowen (1914), is shown as figure 2. The system is binary with a eutectic at 12 per cent forsterite and 1387°. The low slope of

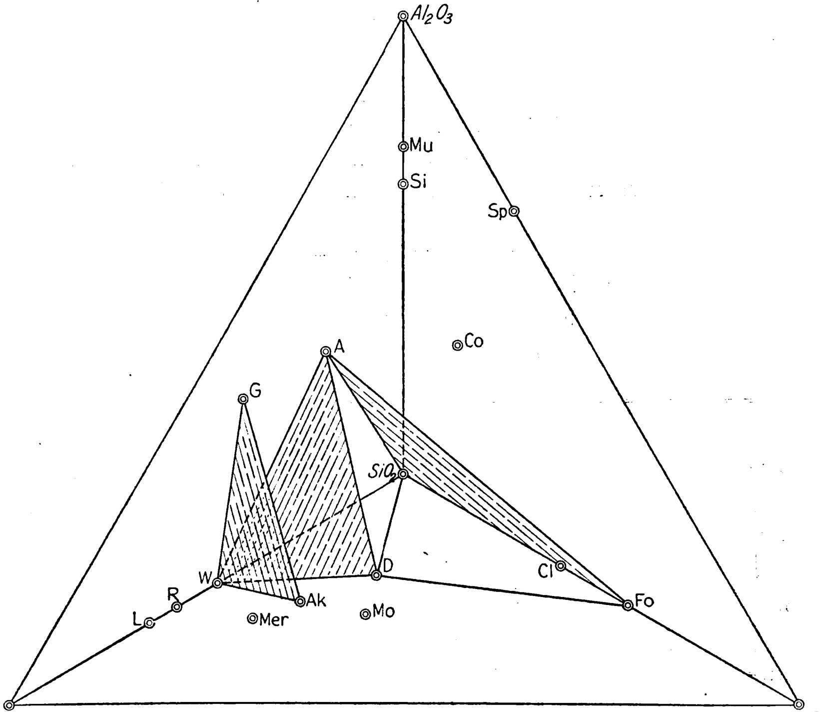

Fig. 1. Diagram representing the quaternary system CaO—MgO—Al_2O_3—SiO_2 as a tetrahedron with one component at each apex. The front face, CaO-MgO-Al_2O_3, has been removed to show the interior of the tetrahedron. Compounds are plotted in weight per cent. L = larnite (Ca_2SiO_4), Mer = merwinite ($Ca_3MgSi_2O_8$), Mo = monticellite ($CaMgSiO_4$), Fo = forsterite (Mg_2SiO_4), R = rankinite ($Ca_3Si_2O_7$), Ak = akermanite ($Ca_2MgSi_2O_7$), W = wollastonite ($CaSiO_3$), D = diopside ($CaMgSi_2O_6$), Cl = clinoenstatite ($MgSiO_3$), G = gehlenite ($Ca_2Al_2SiO_7$), A = anorthite ($CaAl_2Si_2O_8$), Co = cordierite ($Mg_2Al_4Si_5O_{18}$), Sp = spinel ($MgAl_2O_4$), Si = sillimanite (Al_2SiO_5), Mu = mullite ($Al_6Si_2O_{13}$) (after Osborn).

the diopside liquidus curve and the position of the eutectic near the diopside end are noteworthy features of the diagram.

Liquidus relations in the system forsterite—anorthite were investigated by Andersen (1915, p. 424), who found that over a certain composition range, spinel is the primary phase. Consequently, the system is not entirely binary. In the present study quenching data were obtained for six mixtures in order to extend phase data to solidus temperatures (table 1). An equilibrium diagram for the join forsterite-anorthite is shown as figure 3. Points A and B have the same compositions, and B the same temperature, as determined by Andersen (1915, p. 424). Point A is shown as 1475°±5°, as compared with Andersen's temperature of 1466°±4°. Point C may be viewed as a peritectic point for the system anorthite—forsterite—spinel. Its temperature of 1320° ± 5° therefore represents a maximum temperature on the quaternary univariant line along which anorthite, forsterite, spinel and liquid are in equilibrium. The temperature must drop in passing along this line toward point K in the system forsterite—anorthite—silica (Andersen, 1915, fig. 9, p. 437) and in the opposite direction toward point D of figure 5. The temperature gradient along this line, however, is very low inasmuch as points K and D were found to be 1320°

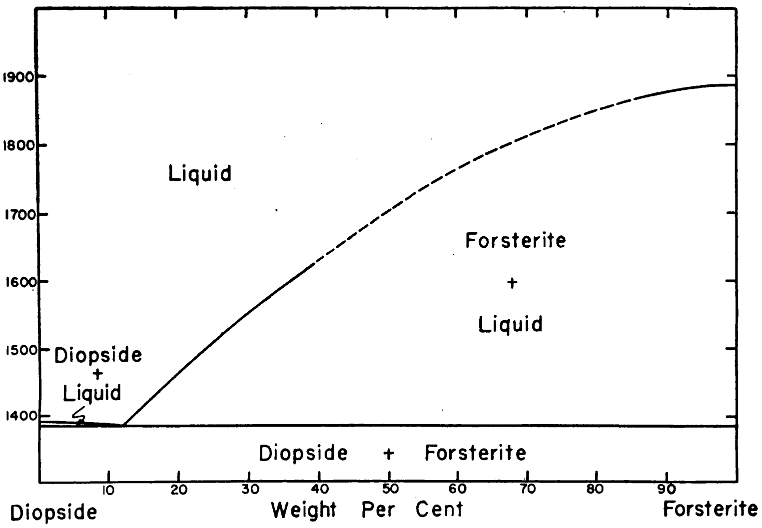

Fig. 2. Equilibrium diagram of the system diopside—forsterite (after Bowen).

(Andersen, 1915, p. 437) and 1317° respectively. Along the curves AC and BC of figure 3, spinel crystallizes from the liquid along with forsterite or anorthite as temperature drops, but at point C as the temperature remains constant and heat is withdrawn from the system, spinel dissolves as anorthite and forsterite crystallize. Below 1320°, only anorthite and forsterite are present under equilibrium conditions.

An equilibrium diagram for the system diopside—anorthite is shown as figure 4, after Osborn (1942, p. 758). The system is believed to be not completely binary, as suggested by the slight slope of the dashed line, probably because the diopside present contains a small amount of Al^{3+} occupying Mg^{2+} and Si^{4+} positions in the structure.

TABLE 1

Summary of Quench Data for the Forsterite-Anorthite Join

Composition in wt. %		Temp.	Time	
Anorthite	Forsterite	(°C.)	(hrs.)	Phase Present*
45	55	1553	15	Fo and glass
45	55	1559	2	glass
54	46	1474	3	Fo, Sp and glass
54	46	1477	2	Fo and glass
54	46	1481	7	glass
60	40	1316	4	Fo and An
60	40	1321	10	Fo, Sp and glass
60	40	1435	1	Fo, Sp and glass
60	40	1441	1	Sp and glass
60	40	1479	2	Sp and glass
60	40	1496	10	glass
80	20	1316	4	Fo and An
80	20	1321	10	An, Sp and glass
80	20	1388	1	Sp and glass
80	20	1412	1	Sp and glass
80	20	1459	2	Sp and glass
80	20	1461	4	glass
86	14	1445	2	An and glass
86	14	1450	1	glass
95	5	1495	3	An and glass
95	5	1500	3	glass

* Fo = crystals of forsterite,
Sp = crystals of spinel,
An = crystals of anorthite.

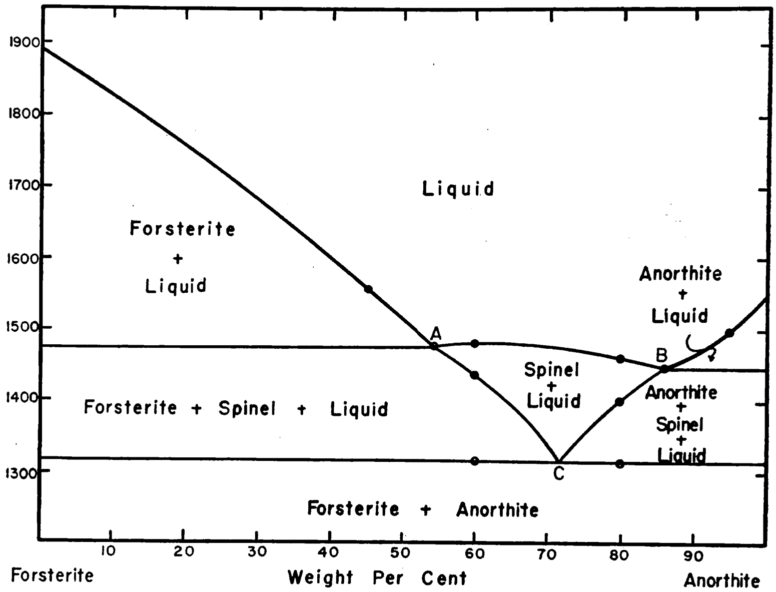

Fig. 3. Equilibrium diagram for the join forsterite-anorthite, a modification of Andersen's diagram to show sub-liquidus relationships.

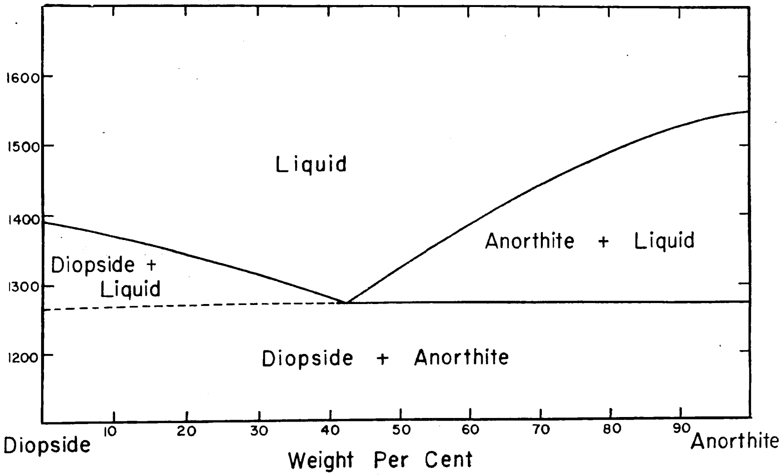

Fig. 4. Equilibrium diagram of the system diopside—anorthite (after Osborn).

QUENCHING RESULTS FOR THE SYSTEM DIOPSIDE—FORSTERITE—ANORTHITE

Data for the system diopside—forsterite—anorthite are summarized in table 2. They are the results of quenching experiments on the 40 mixtures whose compositions are shown by dots in figure 5.

The minimum liquidus temperature in the system, 1270° ± 5°, is that of point E (fig. 5), having the composition in weight per cent, 43.5 anorthite, 49 diopside, and 7.5 forsterite. This point resembles a eutectic, and for most purposes can be treated as such, but the diopside present in equilibrium with anorthite, forsterite, and liquid is presumed to contain a small amount of Al^{3+} on the basis of data for the system diopside—anorthite (Osborn, 1942, p. 758). Since the composition of the diopside crystals in equilibrium with liquid E cannot be represented by a point in the plane of figure 5, point E is not a ternary invari-

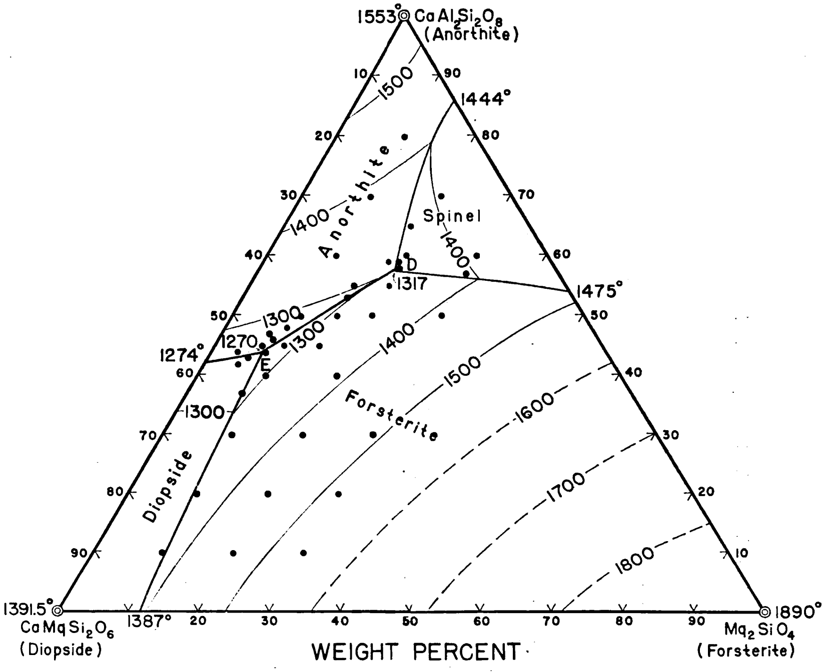

Fig. 5. Equilibrium diagram of the system diopside—forsterite—anorthite. Dots represent compositions of mixtures studied; light lines are isotherms; heavier lines are boundary curves.

TABLE 2

Summary of Quench Data for the System Diopside—Forsterite—Anorthite

Composition in wt. %			Temp. (°C.)	Time (hrs.)	Phase Present*
Anorthite	Diopside	Forsterite			
44	52	4	1277	13	An and glass
44	52	4	1280	2	glass
42	53	5	1278	14	An and glass
42	53	5	1282	2	glass
43	51	6	1274	3	An, Di and glass
43	51	6	1276	13	glass
47	46	7	1285	2	An and glass
47	46	7	1288	10	glass
45	48	7	1278	3	An and glass
45	48	7	1282	5	glass
46	46	8	1291	11	An and glass
46	46	8	1285	3	glass
44	48	8	1270	4	Essentially all crystalline
44	48	8	1274	3	Fo, An and glass
44	48	8	1276	13	glass
37	55	8	1286	3	Di and glass
37	55	8	1289	2	glass
48	43	9	1288	10	An and glass
48	43	9	1293	2	glass
80	10	10	1443	2	An and glass
80	10	10	1445	2	glass
70	20	10	1389	2	An and glass
70	20	10	1395	16	glass
60	30	10	1350	3	An and glass
60	30	10	1355	2	glass
50	40	10	1294	3	An and glass
50	40	10	1297	3	glass
45	45	10	1280	2	Fo and glass
45	45	10	1283	2	glass

* An = crystals of anorthite,
Fo = crystals of forsterite,
Di = crystals of diopside,
Sp = crystals of spinel.

TABLE 2 (Cont.)

Summary of Quench Data for the System Diopside—Forsterite—Anorthite

Composition in wt. %			Temp.	Time	
Anorthite	Diopside	Forsterite	(°C.)	(hrs.)	Phase Present*
40	50	10	1299	2	Fo and glass
40	50	10	1303	2	glass
30	60	10	1340	2	Fo and glass
30	60	10	1342	3	glass
20	70	10	1345	2	Di, Fo and glass
20	70	10	1347	11	Fo and glass
20	70	10	1351	2	glass
10	80	10	1365	13	Di and glass
10	80	10	1371	2	glass
55	30	15	1303	2	An and glass
55	30	15	1306	2	glass
53	32	15	1300	3	Fo, An and glass
53	32	15	1303	4	glass
50	35	15	1303	2	Fo and glass
50	35	15	1306	4	glass
45	40	15	1309	2	Fo and glass
45	40	15	1314	2	glass
65	17	18	1355	2	Sp, An and glass
65	17	18	1362	2	Sp and glass
65	17	18	1370	2	glass
59	23	18	1322	2	An and glass
59	23	18	1327	2	glass
59	21.5	19.5	1325	2	Fo, An and Sp
59	21.5	19.5	1337	2	glass
70	10	20	1411	2	Sp and glass
70	10	20	1415	2	glass
60	20	20	1348	2	Sp and glass
60	20	20	1351	2	glass
58	22	20	1317	2	An, Fo and glass
58	22	20	1324	2	Sp and glass
58	22	20	1327	5	glass

* An = crystals of anorthite,
Fo = crystals of forsterite,
Di = crystals of diopside,
Sp = crystals of spinel.

TABLE 2 (Cont.)

Summary of Quench Data for the System Diopside—Forsterite—Anorthite

Composition in wt. %			Temp.	Time	
Anorthite	Diopside	Forsterite	(°C.)	(hrs.)	Phase Present*
55	25	20	1324	2	Fo and glass
55	25	20	1328	2	glass
50	30	20	1350	3	Fo and glass
50	30	20	1351	2	glass
40	40	20	1365	13	Fo and glass
40	40	20	1371	2	glass
30	50	20	1415	2	Fo and glass
30	50	20	1423	5	glass
20	60	20	1423	5	Fo and glass
20	60	20	1429	3	glass
10	70	20	1445	2	Fo and glass
10	70	20	1449	2	glass
60	10	30	1422	2	Sp and glass
60	10	30	1426	2	glass
57	13	30	1380	2	Fo, Sp and glass
57	13	30	1407	2	rare Sp
50	20	30	1436	3	Fo and glass
50	20	30	1422	2	glass
30	40	30	1458	6	Fo and glass
30	40	30	1463	5	glass
20	50	30	1481	7	Fo and glass
20	50	30	1486	10	glass
10	60	30	1518	3	Fo and glass
10	60	30	1524	2	glass

* An = crystals of anorthite,
Fo = crystals of forsterite,
Di = crystals of diopside,
Sp = crystals of spinel.

ant point. Following Schairer (1942, p. 253), it may be called a piercing point.

The point D in figure 5 (1317° ± 5°) is also a piercing point, representing the intersection of a quaternary univariant line with the plane diopside-forsterite-anorthite. At this point, a liquid of composition D is in equilibrium with anorthite, forsterite, and spinel.

Just as the point D is not invariant, the lines bounding the field of spinel (lighter lines of fig. 5) are not univariant curves, but are the intersections with the plane diopside-forsterite-anorthite of quaternary divariant surfaces.

COURSES OF CRYSTALLIZATION

Equilibrium crystallization.—If as a first approximation point E is considered to be a ternary eutectic, courses of crystallization for mixtures within the area XDZY (fig. 6), of the system diopside—forsterite—anorthite, are of a simple ternary nature. As any liquid within this area is cooled under equilibrium conditions, the composition of the liquid changes as a consequence of the precipitation of crystals of one or more of X, Y, and Z and eventually has the composition E. As the temperature is lowered below 1270°, liquid disappears. Actually, however, diopside occurring in this system is believed not to have a composition accurately represented by the formula $CaMgSi_2O_6$, as stated above. This fact does not materially affect the nature of courses of crystallization, but has the effect of causing those liquids in equilibrium with diopside to lie slightly outside the plane of the diagram, i.e., to have compositions not accurately represented by mixtures of X, Y, and Z.

During the equilibrium crystallization of liquids within the area XDZ (fig. 6), the composition of the liquid at a certain temperature leaves the plane of the diagram (ceases to have a composition represented by mixtures of X, Y, and Z), after a temperature drop returns to the plane at point D, and with a further decrease in temperature moves to point E along the ternary boundary curve DE. This may be illustrated by noting the history of two representative points *a* and *c* (fig. 6) during their cooling from the liquidus to the solidus temperature.

Assuming that equilibrium among the phases is maintained, crystals of forsterite separate from liquid *a* as it is cooled from the liquidus temperature (1500°). The continued crystallization of forsterite from the liquid causes the composition of the latter to change along a straight line from *a* to *b*. At *b* (1400°) crystals of spinel appear. The point representing the composition of spinel (fig. 1) does not lie on an extension in the tetrahedron of the plane diopside-forsterite-anorthite, but instead lies forward (toward the CaO-Al_2O_3-MgO face) of this plane.[3] Therefore, as the temperature is lowered below that of point *b*, the coprecipitation of spinel and forsterite causes the liquid to leave the D-Fo-A plane (fig. 1), moving behind (on the SiO_2 side of) the plane, in a direction away from forsterite and spinel. With continued decreasing temperature, the liquid therefore follows the forsterite-spinel divariant surface, with both spinel and forsterite precipitating, until the forsterite-spinel-anorthite univariant line is reached. The liquid reaches this line at a temperature between 1320° and 1317°, and at a position on this line between point C (fig. 3) and point D (fig. 6). The liquid then, with decreasing temperature, moves along this univariant line toward D as spinel dissolves and forsterite and anorthite crystallize. Just as point D is reached (1317°), the last of the spinel crystals disappear and the liquid moves down DE to E (fig. 6) as anorthite and forsterite continue to crystallize. At E, diopside, forsterite, and anorthite crystallize together as the liquid is consumed.

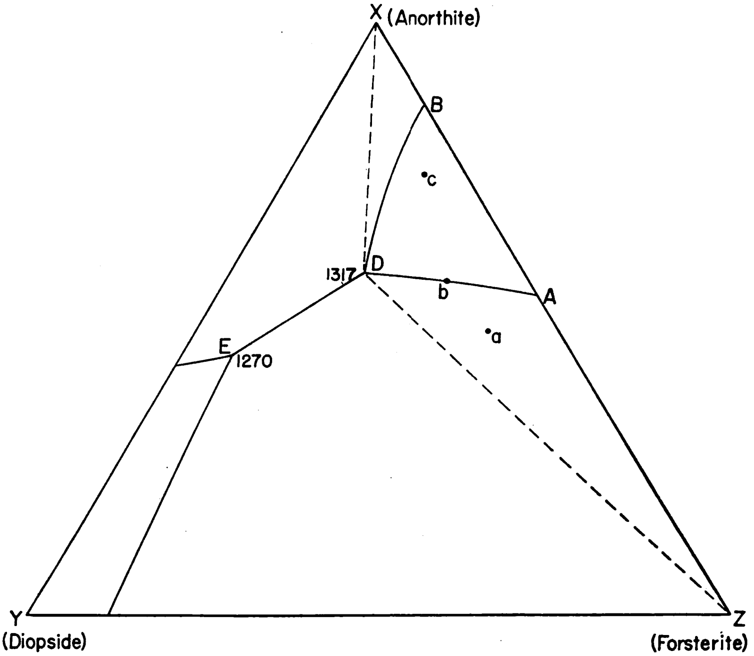

Fig. 6. Sketch of the system diopside—forsterite—anorthite to illustrate courses of crystallization.

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[3] This is true also if the composition of the spinel phase lies between $MgAl_2O_4$ and Al_2O_3.

On the equilibrium cooling of liquid *c* spinel crystals appear at 1425°. The continued separation of spinel crystals with cooling causes the composition of the liquid to leave the plane XYZ (fig. 6), passing into the tetrahedral volume D-A-Fo-SiO_2 (fig. 1), where it intersects the divariant surface spinel-anorthite. These two crystalline phases then coprecipitate with decreasing temperature as the liquid moves to the diopside-forsterite-anorthite univariant line, reaching this line at a temperature between 1320° and 1317°. The subsequent history of the liquid with further cooling is similar to that of the liquid of mixture *a* in this temperature range.

Fractional crystallization.—Owing to the fact that spinel is a transient phase in the system diopside—forsterite—anorthite, and further that as a consequence of the crystallization of spinel the composition of the liquid leaves this plane to enter the tetrahedron D-A-Fo-SiO_2 (fig. 1), it is of interest to note the course of crystallization of a mixture such as *a* (fig. 6) when equilibrium is not maintained. For this purpose, let us consider the system diopside—forsterite—anorthite—silica, as sketched in figure 7.

In figure 7 the system diopside—forsterite—anorthite—silica is shown as a tetrahedron with the front face removed, reduced in size, and moved to the right. Boundary curves, invariant points, and piercing points, with their respective temperatures, are shown on each face. It can be seen that three quaternary univariant lines, depicted schematically in the lower part of figure 7, pass through this tetrahedron, and that no quaternary invariant points are present. One line, along which anorthite, forsterite, and spinel are in equilibrium with liquid, joins two piercing points, one located on the right face and one on the front face. This is a line of low temperature gradient and it possesses a temperature maximum at a point corresponding to C of figure 3. A second line, anorthite-pyroxene-forsterite, extends from the peritectic on the right face to the "eutectic" on the front face. A temperature minimum occurs on this line near the front face. A third line joins the eutectic on the right face with that on the left face. The arrows on the line indicate a temperature minimum also on this line, near the left end. Data are not available to prove this, but it is probable that such a temperature minimum exists.

As mixture *a* (fig. 6) is cooled to a temperature below that of *b*, spinel and forsterite crystallize together out of the liquid as the composition of the liquid moves from the front face (fig. 7) into the tetrahedron toward the univariant line An-Fo-Sp reaching this line at a point to the left of the maximum on the line. The liquid can remain on this univariant line with decreasing temperature only if spinel dissolves as forsterite and anorthite crystallize. If the spinel does not dissolve, as would be the case in perfect fractional crystallization where a crystal as soon as formed is effectively removed from the system, the liquid leaves the line as forsterite and anorthite continue to crystallize, and follows the forsterite-anorthite divariant surface

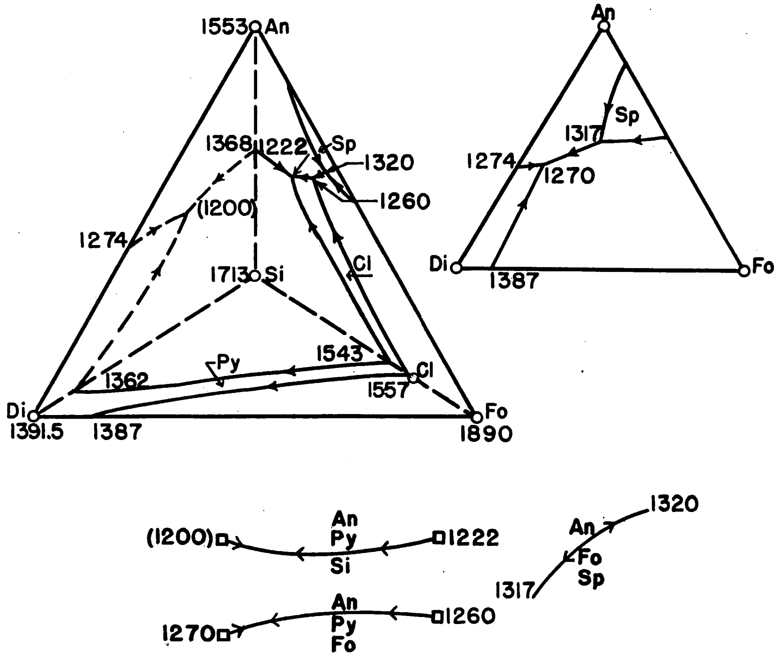

Fig. 7. Sketch to illustrate phase equilibrium relations in the system diopside—forsterite—anorthite—silica. The system is shown as a regular tetrahedron with the front face removed, reduced in size and shown at the right. The position of compounds and of boundary curves on the faces are indicated. In the lower part of the figure, the three univariant lines which pass through the tetrahedron are shown schematically, with the three crystalline phases indicated which exist in equilibrium with liquids along the line. The temperature of 1200°, shown in parentheses, is the approximate metastable eutectic of cristobolite, diopside, and anorthite, after Greig. Di = diopside, Fo = forsterite, An = anorthite, Si = silica, Cl = clinoenstatite, Py = pyroxene, and Sp = spinel.

to the second univariant line (An-Py-Fo) where a pyroxene (aluminous diopside-clinoenstatite solid solution) begins to crystallize. At this stage (about 1250°) the liquid therefore contains crystals of forsterite, pyroxene, anorthite, and spinel. If the An-Py-Fo univariant line passes inside, and not outside of the triangle whose apices are points representing the composition of forsterite, anorthite, and the pyroxene precipitating, then forsterite, pyroxene, and anorthite crystallize together as the liquid moves toward the temperature minimum and disappears. The failure of spinel to react with the liquid and disappear as anorthite and forsterite crystallize thus causes the final liquid of this crystallizing mixture to have a higher silica content than that of point E (fig. 6). Furthermore, it is possible that the pyroxene, which begins to crystallize as the liquid in mixture *a* reaches the univariant line An-Py-Fo (fig. 7), has a composition such that this univariant line passes outside the anorthite-forsterite-pyroxene composition triangle.[4] In this case part of the forsterite would react with the liquid and disappear as pyroxene and anorthite crystallize if equilibrium among anorthite, forsterite, pyroxene, and liquid were maintained as the liquid cooled. But we are considering extreme fractionation in which solution of a crystalline phase (spinel or forsterite) does not occur on cooling. Just as in the case of the failure of spinel to dissolve as anorthite and forsterite crystallize, the failure of forsterite to react with the liquid and partly disappear forces the liquid to leave a univariant line (An-Py-Fo), to move along the anorthite-pyroxene divariant surface as these two phases separate, and to reach the An-Py-Si univariant line (fig. 7) at a temperature of about 1200°. With subsequent cooling, silica

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[4] Data on the composition of pyroxenes in equilibrium with anorthite, forsterite, and liquid are not available to show for what mixtures this may be true. Pyroxenes appearing during the fractional crystallization of mixture *a* (fig. 7) probably have compositions such that forsterite will crystallize along with pyroxene. But undoubtedly the pyroxene appearing during the fractional crystallization of some mixtures in the system diopside—forsterite—anorthite—silica from which spinel precipitates as the primary or secondary phase has a composition such that the forsterite structure, with equilibrium crystallization, must disappear as pyroxene crystallizes. Indeed, this is probably the general case in view of the relations in the system forsterite—anorthite—silica wherein: (a) the pyroxene present is the end member, clinoenstatite; and (b) the area in which olivine appears as the primary phase, but later must completely disappear with equilibrium crystallization, is about three times as large as the similar area in the system forsterite—diopside—silica.

crystallizes along with anorthite and pyroxene until the liquid disappears. The final aggregate is composed of spinel, forsterite, anorthite, pyroxene, and silica.

DISCUSSION

During the crystallization and differentiation of natural magmas, eutectic relations among phases must rarely if ever exist owing to the important role of solid solution and incongruent melting phenomena. In simple silicate systems, eutectics are common, but as these systems are complicated by the addition of other components, particularly if the composition is shifted toward that of natural magmas, eutectics play a less important role in the crystallization. The ternary system diopside—forsterite—silica, for example, which is sketched on the base of figure 7, is bounded by three binary systems each of which contains a eutectic, but in the ternary system no eutectic or other invariant point exists. In some other ternary systems of petrologic significance, such as the systems MgO—FeO—SiO_2 (Bowen and Schairer, 1935) and $NaAlSiO_4$—$KAlSiO_4$—SiO_2 (Schairer and Bowen, 1935), the same presence of eutectics in the bounding binary systems and absence of ternary eutectics is noteworthy. Systems approaching natural magmas in composition are thus characterized by reaction during crystallization, wherein a crystalline phase which has precipitated commonly must at a lower temperature react with the liquid and change in composition or dissolve or both. The failure of crystalline phases to react to the extent demanded by phase equilibrium relationships is the basis for the crystallization differentiation of magmas so ably expounded by Bowen (1928).

The system diopside—forsterite—anorthite has as components end members of the three minerals of most importance from a quantitative standpoint in igneous rocks of the earth's crust—pyroxenes, olivines, and feldspars. Yet in this system the three minerals crystallize together essentially as in a eutectic system, and reaction with liquid is virtually absent insofar as these phases are concerned. Similarly, the system diopside—anorthite—silica, shown as the left face in figure 7, has a ternary eutectic at which a pyroxene, a feldspar, and a silica mineral crystallize together from the liquid. But if another component is added to these systems to give the quaternary system diopside—forsterite—anorthite—silica, (fig. 7), quaternary invariant points are non-existent. Three univariant lines cross through the tetrahedron, any point on a univariant line representing the composition of liquid in equilibrium with three crystalline phases. As shown schematically in the lower part of figure 7, the three assemblages of crystalline phases which can exist in mixtures in this system under equilibrium conditions are: anorthite-pyroxene-silica, anorthite-pyroxene-forsterite, and anorthite-forsterite-spinel.

That three crystalline phases are in equilibrium with liquid does not however mean that they are all crystallizing from the liquid as it cools and changes composition along a quaternary univariant line. On the contrary, if equilibrium among the phases is maintained, spinel must dissolve as the liquid moves along the An-Fo-Sp line with decreasing temperature (fig. 7), and forsterite must dissolve over most of the length of the An-Py-Fo line. The composition of the liquid changes only in response to the subtraction of crystals or addition of substances, and for the liquid to change its composition along these lines, spinel and forsterite respectively must dissolve,[5] except along a short length at the left end of the An-Py-Fo line. If spinel in a liquid on the An-Fo-Sp line fails to dissolve at the required rate, as for example, because cooling is too rapid or because spinel crystals have been included in larger forsterite crystals which protect the spinel from attack by liquid, the composition of the liquid leaves the univariant line An-Fo-Sp, moves along the anorthite-forsterite divariant surface as these two phases separate, and reaches the next univariant line, An-Py-Fo. If the composition of the liquid on this line is such that with cooling forsterite should dissolve, then if it fails to do so the liquid leaves this line as anorthite and pyroxene crystallize and moves to the third univariant line. Here tridymite separates along with pyroxene and anorthite until the liquid is exhausted.

The olivine-liquid reaction is one of the well established phenomena on which the formation of igneous rock series by crystallization differentiation is based. The spinel reaction must also play a role during the crystallization of some basaltic magmas. Spinel, as pleonaste or picotite, occurs not uncommonly as primary inclusions in the olivine of basalt. Judging

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[5] If one constructs a tetrahedron of the system $CaO—MgO—Al_2O_3—SiO_2$, it can be clearly seen that spinel and forsterite must dissolve as liquid moves along the An-Fo-Sp and An-Py-Fo lines, respectively, with decreasing temperature.

from the relations in the system diopside—forsterite—anorthite—silica and from the data of Schairer (1942, pp. 250-253) on the system anorthite—fayalite—silica in which hercynite appears as a transient phase just as does spinel in the former system, the pleonaste or picotite once formed in a basaltic liquid should at a lower temperature dissolve if equilibrium among the phases were realized. The failure of spinel, once formed, to dissolve during subsequent crystallization would have the same type of effect on liquid composition as the failure of olivine to dissolve, i.e., the residual liquid has a higher silica and a lower magnesia content than would be the case under equilibrium crystallization.

It will be noted from figure 7 that at temperatures above the solidus spinel cannot exist in equilibrium with a pyroxene in the system diopside—forsterite—anorthite—silica. Further, in this system diopside and clinoenstatite cannot coexist in equilibrium with liquid, but rather a solid solution of the two end members will form. On the other hand, anorthite and forsterite are compatible phases, as must also be calcic plagioclase and magnesian olivine, at least at high temperatures.

Troctolites, which are composed almost entirely of these latter two minerals, were described recently by Osborne (1949). Of special interest is the abundant growth of secondary, or reaction minerals in the troctolite, replacing the original plagioclase and olivine. The reaction minerals are dominantly a diopsidic pyroxene, enstatite, and spinel, with diopside and spinel commonly forming wormy intergrowths. The conclusions would seem to be: (1) that calcic plagioclase and magnesian olivine are not compatible within a temperature range existing below that of figure 7, (2) that in this lower temperature range spinel and diopside can coexist in equilibrium and (3) that this temperature range is also below the inversion temperature of enstatite to clinoenstatite (1145°) (Bowen and Schairer, 1935, p. 168) and is probably a few hundred degrees below this inversion temperature inasmuch as the inversion of enstatite plus diopsidic pyroxene to a diopside-clinoenstatite solid solution must occur at a lower temperature than the inversion of enstatite to clinoenstatite. Figure 7 therefore pertains to high temperature reactions such as the crystallization of plagioclase and olivine from a basaltic liquid and their settling and accumulating to form a mass of troctolite. At lower temperatures, below a maximum of perhaps 900°C., the fields of spinel and diopside probably adjoin, as the fields of anorthite and forsterite cease to be contiguous.

In conclusion and referring to figure 5, the profound effect on the temperature of development of liquid in a forsterite body caused by small additions of lime, alumina, and silica may be noted. Liquid will appear at 1270°C. But it may also be observed that the eutectic lies close to the side line opposite the forsterite apex. At 1270° or at somewhat higher temperatures, the amount of liquid generated because of the presence of small amounts of these oxides will be small.

SUMMARY

The system forsterite—diopside—anorthite possesses a liquidus temperature minimum, which as a first approximation is a ternary eutectic, at 1270°C. where the three crystalline phases are in equilibrium with a liquid of the composition in weight per cent: 7.5 forsterite, 49 diopside, 43.5 anorthite. A field of spinel intrudes the system in view of the incompatibility of forsterite and anorthite at high temperatures. At temperatures between 1317° and 1270°C., however, spinel is not a stable phase in mixtures in this system, but instead forsterite and anorthite coexist.

The system forsterite—diopside—anorthite may be viewed as a triangular join within a tetrahedron representing the quaternary system CaO—MgO—Al_2O_3—SiO_2. As such, it is one face of an interior tetrahedron (diopside-forsterite-anorthite-silica) from whose liquids forsterite, anorthite, diopside-clinoenstatite solid solutions, spinel, and silica minerals crystallize. Although spinel crystallizes from liquids of this interior tetrahedron over a rather wide range of composition and temperature, it must at lower temperatures always react with the liquid and disappear if equilibrium is maintained. Failure of this spinel-liquid reaction to go to completion will cause the final liquid to be enriched in silica over its equilibrium composition, just as in the familiar case of the forsterite-liquid reaction. From previous work on iron silicate systems, it may be judged that this same situation obtains if ferrous ions are present in the spinel and olivine. The occurrence of spinel as inclusions in the olivine of basalt suggests that the spinel-liquid reaction is commonly deterred by the precipitation of an olivine layer about spinel crystals.

At temperatures above the solidus in the system forsterite—diopside—anorthite—silica, either forsterite, anorthite, and spinel, or forsterite, anorthite and pyroxene may coexist in equilibrium but pyroxene and spinel are not compatible. Field and laboratory studies of troctolite and associated coronite suggest, however, that at lower temperatures these relationships are reversed, i.e., spinel and diopside coexist under equilibrium conditions but not calcic plagioclase and olivine. Therefore, at some moderate temperature an accumulation of calcic plagioclase and magnesian olivine crystals becomes a metastable assemblage which will, if conditions are appropriate, transform to the low temperature stable assemblage of pyroxene, spinel, and plagioclase or pyroxene, spinel and olivine. Thus, available evidence suggests that both at high temperatures (above about 1320°) and at low temperatures (below about 900°) calcic anorthite and magnesian olivine constitute a metastable assemblage, but that at intermediate temperatures they may coexist at equilibrium.

ACKNOWLEDGMENTS

Most of the mixtures used in this study were prepared by the senior author in 1940 and 1941 while on the staff of the Geophysical Laboratory of the Carnegie Institution of Washington. The writers wish to thank Dr. L. H. Adams, Director of the Geophysical Laboratory, for releasing samples of these preparations for further study at The Pennsylvania State College.

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