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## REACTION SERIES FOR SUBALKALINE IGNEOUS ROCKS BASED ON DIFFERENT OXYGEN PRESSURE CONDITIONS<sup>1</sup>

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### ABSTRACT

Two reaction series schemes are constructed by building on Bowen's "Reaction Series in Subalkaline Rocks," and using recent phase equilibrium data for the system MgO-CaO-FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>. Both schemes have a discontinuous series of ferromagnesian minerals and the continuous series of lime-soda feldspars. In the first, where oxygen pressure remains at a high level during fractional crystallization of a basaltic liquid, magnetite coprecipitates with members of the other series, and the residual liquid is silica-rich. This scheme applies to common calc-alkaline rock series of orogenic belts. In the second scheme where oxygen pressure is much lower, iron-olivine crystallizes rather than magnetite, and the residual liquid is FeO-rich. Fractional crystallization according to the latter scheme develops rock series of the gabbroic, layered intrusion type.

### INTRODUCTION

Four decades ago a former president of our Society published a paper on the reaction principle in petrogenesis (Bowen, 1922). The purpose was to direct attention to the importance of *reaction relations* among minerals of igneous rocks in providing opportunities for differentiation, in contrast to the *eutectic type* of relation. He pointed out that there are two distinct types of reaction relations. The first of these is that shown by all solid solution series. This he called a *continuous reaction series*. The second is that between the phases involved in incongruent melting. Two crystalline phases involved in incongruent melting he spoke of as a reaction pair, and with three or more crystalline phases the result is a *discontinuous reaction series*.

In Fig. 1 is a reproduction of Bowen's diagrammatic outline of the reaction series for subalkaline rocks. He stated that "neither rigid accuracy nor finality is claimed. It is regarded merely as a framework upon which others may build, making such modifications and additions as may be found necessary" (Bowen, 1922). In later reference to this reac-

<sup>1</sup> Address of retiring President of the Mineralogical Society of America at the 42nd annual meeting of the Society at Cincinnati, Ohio, November 3, 1961. Original title was "Two Reaction Series."

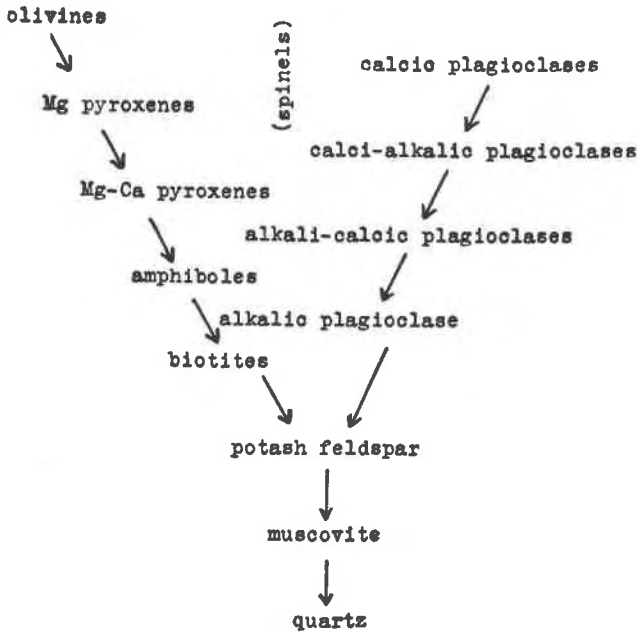


FIG. 1. Reaction series in subalkaline rocks, after Bowen (1922).

tion series scheme he added: "The matter is really too complex to be presented in such simple form. Nevertheless the simplicity, while somewhat misleading, may prove of service in presenting the subject in concrete form" (Bowen, 1928).

The basis for the reaction series was largely petrographic, with support from experimental work. The continuous series of plagioclase feldspars on the right in Fig. 1 was established on the basis of observations on rocks as well as from Bowen's phase diagram for this series of silicate solid solutions (Bowen, 1913). Evidence for the verity of the discontinuous series representing the left arm of Fig. 1 was less definite. It was based almost entirely on petrographic studies of rocks but with some support from the experimentally established forsterite-clinoenstatite reaction relation (Bowen and Andersen, 1914).

Phase equilibrium diagrams for two ternary systems had been published prior to 1922 which had an important bearing on this matter. One was for the system anorthite-albite-diopside (Bowen, 1915), and the other for the system forsterite-silica-diopside (Bowen, 1914). These are sketched in Fig. 2(a) and (b) where circles represent areas of haplobasaltic<sup>1</sup> composition. These diagrams depict liquidus relations. Each field

<sup>1</sup> The term "haplobasaltic" was coined by Bowen (1915) to mean "simple basaltic."

represents the composition range of liquids that can coexist in equilibrium with the crystalline phase indicated by the label. The solid lines are boundary curves, representing compositions of liquids in equilibrium with two crystalline phases. To keep the diagrams simple isotherms have been omitted, but arrows show the direction of decreasing temperature along the boundary curves. It is noteworthy that in each of these systems, and also in the third to be discussed later, the only eutectics that occur are those in the binary side lines of the diagrams. The heavy lines leaving the circles and moving across the diagram represent the path of liquid on extreme fractional crystallization of the haplobasaltic liquid. The dashed lines indicate silica content of the liquids.

By means of diagram (a) of Fig. 2, Bowen illustrated the nature of

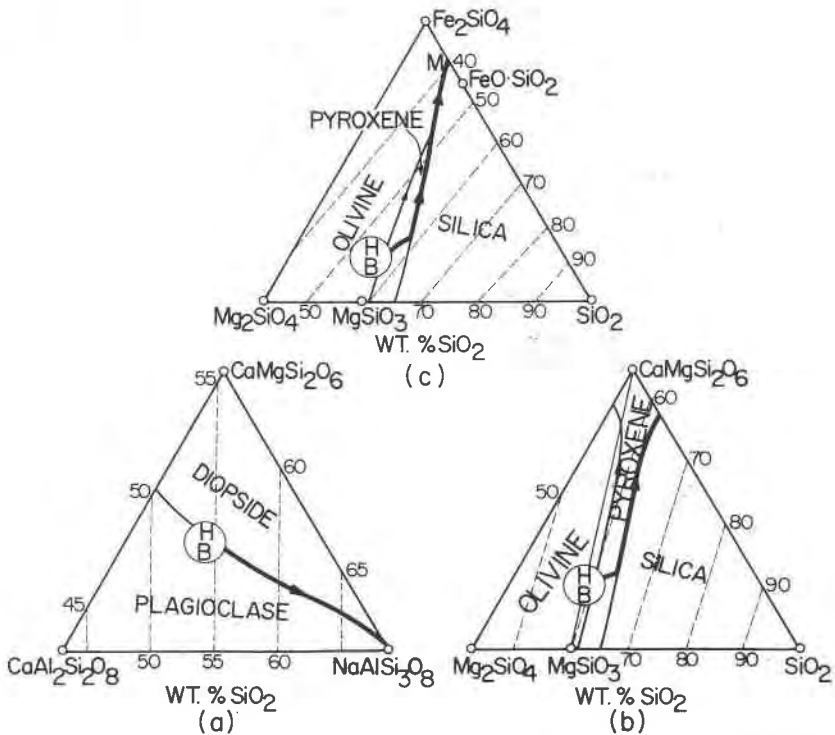


FIG. 2. Equilibrium diagrams for three systems exhibiting phase relations bearing on reaction series in igneous rocks. Diagrams (a) and (b) are after Bowen (1915 and 1914), and diagram (c) after Bowen and Schairer (1935). Circle labeled HB indicates composition of haplobasalt. The heavy, solid line passing from the circle to the right sideline is the course a liquid of initial haplobasaltic composition follows when fractionally crystallized. Lines of equal  $\text{SiO}_2$ -content are shown dashed.

simultaneous crystallization of the continuous plagioclase solid solutions with a pyroxene, thus demonstrating how the essential feature of a continuous reaction series, the reaction relation of crystals and liquid, is retained when the series becomes a part of a more complex system. Cooling of liquid HB from its liquidus temperature causes plagioclase crystals along with diopside to separate. Their separation causes the composition of the liquid to change continuously down the boundary curve, as indicated by the heavy line, toward the  $\text{NaAlSi}_3\text{O}_8$  apex. With extreme fractionation (very small crystals of plagioclase forming, of successively higher Na:Ca and Si:Al ratio, and without subsequent reaction with liquid), the last drop of liquid approaches closely to the composition of this apex and thus has a high silica and soda content.

In diagram (b) of Fig. 2 the phase relations of forsterite, a series of iron-free clinopyroxenes, silica and liquid are illustrated. When a liquid of composition HB is crystallized with a high degree of fractionation, the composition of the liquid follows the course shown by the heavy line, moving in a general direction away from the forsterite apex until silica begins to separate and then following the field boundary curve toward the right sideline. The silica content of the final liquid is slightly higher than that of the original HB liquid.

Returning now to Bowen's diagram outlining his reaction series (Fig. 1), we see that the minerals of the discontinuous series are all iron bearing, and some of them are water bearing. At the time Bowen drew up this series the Geophysical Laboratory had made no equilibrium studies of closely analogous iron-bearing phases. It was not until 1932 that the equilibrium diagram for the system  $\text{FeO-SiO}_2$  appeared (Bowen and Schairer, 1932) followed by those for the systems,  $\text{CaO-FeO-SiO}_2$  (Bowen, Schairer and Posnjak, 1933), and  $\text{MgO-FeO-SiO}_2$  (Bowen and Schairer, 1935). This last study made possible an evaluation of the role of ferrous oxide in the upper, anhydrous part of the discontinuous series. A sketch of the liquidus diagram for the higher silica part of the  $\text{MgO-FeO-SiO}_2$  system is shown as diagram (c) of Fig. 2. Noteworthy is the fact that with fractional crystallization of a liquid lying in the pyroxene or olivine field, the liquid moves to one of the boundary curves and thence on toward the point M on the  $\text{Fe}_2\text{SiO}_4\text{-SiO}_2$  sideline. The actual course the liquid takes in moving from the region of the HB circle to M can be rather complicated, as was thoroughly discussed by the authors, but it will have the general direction as indicated somewhat schematically by the heavy line. A liquid in moving from HB to M decreases in  $\text{SiO}_2$  from about 55% to 38%, while FeO increases from about 10% to 62%. This work raised a question from the experimental side as to whether in the fractional crystallization of basaltic magma the

residual liquid follows the course indicated by Bowen's scheme, or becomes more iron-rich as believed by a number of writers.

During succeeding years, petrologists attempted to apply Bowen's scheme of the reaction series to differentiation of basaltic magma, and encountered difficulties. Evidence accumulated through careful studies of layered intrusions and basalt flows that in such cases the direction of change of liquid composition on fractional crystallization of basaltic magma was not as predicted from Bowen's reaction series, but rather toward increase in iron oxide content without notable increase in silica content. This seemed true at least for early and middle stages of crystallization. Because of this, coupled with concern over the problem of volume relations, many petrologists have largely abandoned the idea that fractional crystallization as depicted in Bowen's reaction series can account for the derivation of the common calc-alkaline series of rocks from basaltic magma. We find this conclusion in the writings of Wager and Deer (1939), Kuno (1950, 1959), Tilley (1950), Wilcox (1954), Waters (1955), Hess (1960), Turner and Verhoogen (1960), and others. These authors suggest contamination of basaltic magma, along with some fractional crystallization, as the mechanism by which the calc-alkaline series of common basalts, andesites, dacites and rhyolites is formed; or partial melting of rocks to give magmas of these compositions is an alternate suggested hypothesis.

Quite apparently the behavior of iron oxide during crystallization is one key to the magma differentiation problem. Iron oxide behavior is strongly influenced by oxygen pressure. A picture of the influence of oxygen pressure on the role of iron oxide during crystallization of silicate melts is gradually emerging. Certain aspects having a bearing on crystallization of basalts have been discussed by Kennedy (1948 and 1955), Muan (1958), Obsorn (1959) and Osborn and Roeder (1960). In the following the problem will be treated by considering the system  $Mg_2SiO_4$ - $CaSiO_3$ -iron oxide- $SiO_2$  under two very different conditions of oxygen pressure. This may serve to help clarify the important role of iron oxide as a determinant of the direction of differentiation during fractional crystallization of a basaltic magma.

#### TWO TETRAHEDRA

Two tetrahedra representing equilibrium conditions in the system  $Mg_2SiO_4$ - $CaSiO_3$ -iron oxide- $SiO_2$  under two different conditions of oxygen pressure are sketched in Figs. 3 and 4. These are liquidus diagrams just as were the triangles in Fig. 2. The liquidus fields on the faces of each tetrahedron extend as volumes into the tetrahedron. Each volume is the liquidus of the crystalline phase indicated by the label,

*i.e.*, it represents the compositions of all liquids which can coexist in equilibrium with the crystalline phase. To illustrate, there is a field labeled pigeonitic pyroxene on the base and left face of each tetrahedron. These fields are the outside boundaries of the pigeonitic pyroxene liquidus

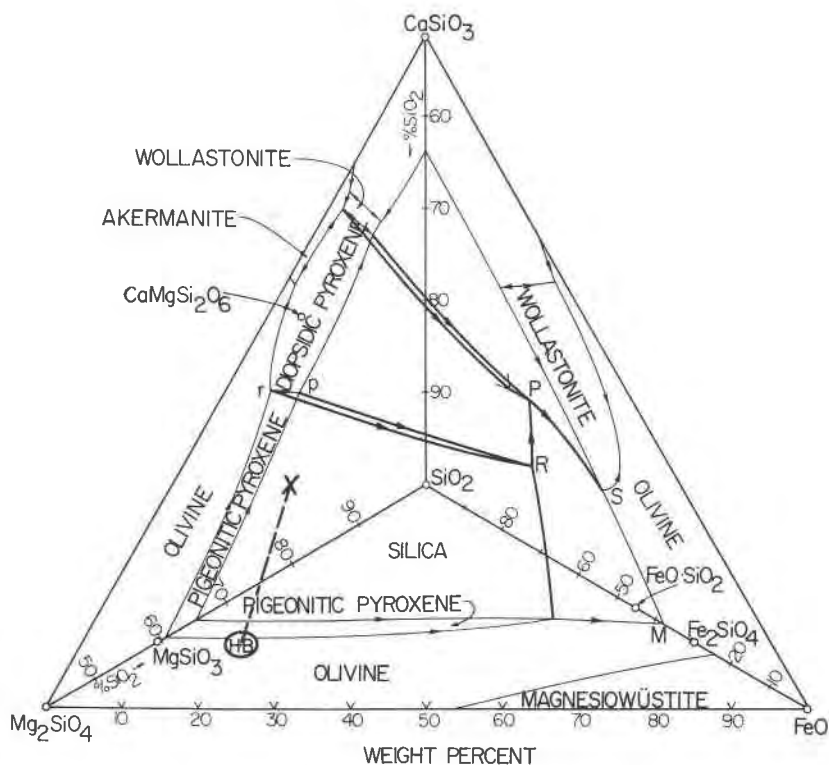


FIG. 3. Tetrahedron to illustrate liquidus phase relations in the system  $Mg_2SiO_4$ - $FeO$ - $CaSiO_3$ - $SiO_2$ . Oxygen pressure very low. Heavy lines represent boundary curves within the tetrahedron along which three crystalline phases are in equilibrium with liquid. Points P and R are quaternary invariant points referred to in the text. This system is quaternary, and these points are invariant only when the small content of  $Fe_2O_3$  is arbitrarily regarded as  $FeO$ . See Bowen and Schairer (1932 and 1935). The two short, dashed lines near P represent two additional quaternary univariant lines which join two others at the quaternary invariant point at which diopsidic pyroxene, olivine, wollastonite and akermanite coexist with liquid. HB on the base is haplobasalt composition as in Fig. 2(c). The point X represents extension of haplobasaltic compositions up into the tetrahedron. Light lines are boundary curves on three faces of the tetrahedron. Arrows on lines indicate direction of decreasing temperature. Figures on the three edges of the tetrahedron radiating from the  $SiO_2$  apex show weight percent  $SiO_2$ . The left face is principally after Bowen (1914), Schairer and Bowen (1942) and Osborn and Muan (1960). The base is after Bowen and Schairer (1935). The right face is after Bowen, Schairer and Posnjak (1933).

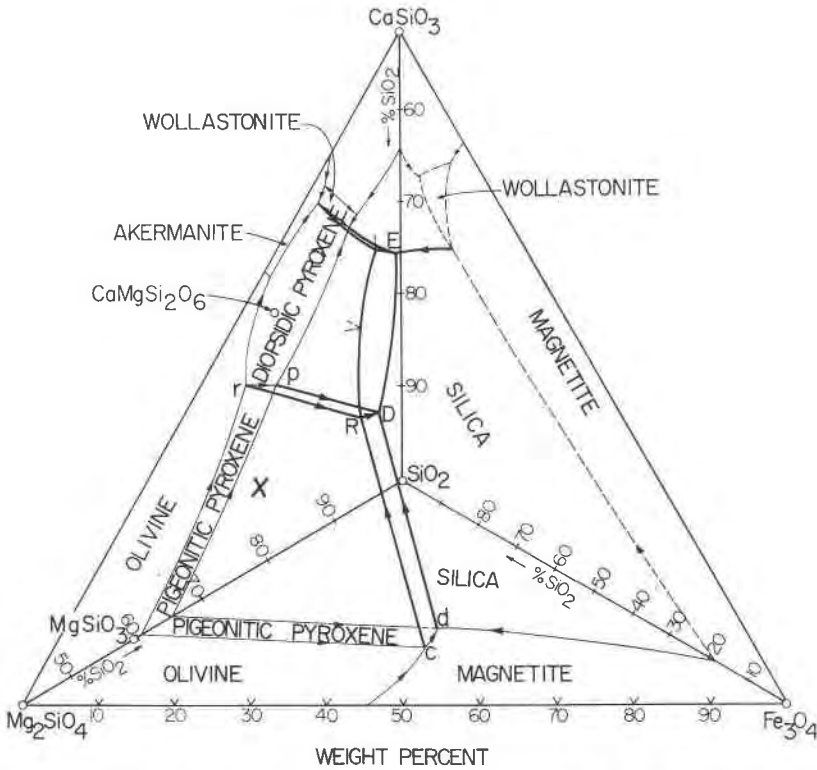


FIG. 4. Tetrahedron to illustrate liquidus phase relations in the system  $Mg_2SiO_4$ -iron oxide- $CaSiO_3$ - $SiO_2$  at a constant oxygen pressure of 0.21 atm. Heavy lines are univariant lines, and points R, D and E are invariant points within the constant oxygen pressure tetrahedron. This tetrahedron represents equilibrium relations existing among the condensed phases in a part of the five-component system Ca-Mg-Si-Fe-O at an oxygen pressure of 0.21 atm. Equilibrium therefore is univariant along these lines inasmuch as five phases (3 crystalline, 1 liquid, 1 gas) coexist at the fixed oxygen pressure. Invariant equilibrium is present at the points because six phases coexist at the fixed oxygen pressure. The short dashed, light line near E and the two between R and E represent segments of univariant lines of little interest in this study. The point X has a significance similar to that for X in Fig. 3. Figures on the three edges of the tetrahedron radiating from the  $SiO_2$  apex show weight per cent  $SiO_2$ . The left face is principally after Bowen (1914), Schairer and Bowen (1942) and Osborn and Muan (1960). The base is after Muan and Osborn (1956). Relations in the right face are inferred.

volume existing within the tetrahedron. Each point in this volume represents the composition of a liquid that can coexist in equilibrium with pigeonitic pyroxene, and only with pigeonitic pyroxene. The temperature of this possible equilibrium, not shown on the diagram, is the liquidus temperature for this composition. Above the pigeonitic pyroxene liquidus

volume is the liquidus volume of diopsidic pyroxene, which similarly represents compositions of all liquids which can coexist only with this crystalline phase. Behind the pyroxene liquidus volumes is the silica liquidus volume, and in front the olivine liquidus volume. It will be evident from what has been said that a surface in which two liquidus volumes meet, being common to the liquidus volumes of two crystalline phases, must represent the compositions of all liquids that can coexist in equilibrium with both of these crystalline phases. Similarly a line in which the liquidus volumes of three crystalline phases meet represents the compositions of all liquids that can coexist in equilibrium with the three crystalline phases; and a point in which four such lines, and also of course four volumes meet represents the composition of a liquid that can coexist in equilibrium with the four indicated crystalline phases.

Both tetrahedra have as apices: silica, magnesium orthosilicate, calcium metasilicate, and iron oxide, FeO in Fig. 3, and Fe<sub>3</sub>O<sub>4</sub> in Fig. 4. It will be seen that the volumes and their spacial relations differ somewhat in the two. This difference is caused by the difference in the oxygen pressures under which the equilibria represented occur. Figure 3 shows relations at the very low oxygen pressures under which the phases can coexist with metallic iron, while Fig. 4 shows relations under a constant oxygen pressure equal to that of the oxygen in air at one atmosphere. In the former the iron oxide apex is shown as FeO, in the latter as Fe<sub>3</sub>O<sub>4</sub>. The use of these two oxides to indicate the iron oxide apex is for convenience in representation. Actually ferric oxide is present in the liquids of Fig. 3, and liquids of Fig. 4 do not maintain a 1:1 ratio of FeO:Fe<sub>2</sub>O<sub>3</sub>; but in each case the iron oxide designation at the apex indicates the approximate oxidation state of the iron in liquids at liquidus temperatures. The phase relations as shown within the tetrahedra are as estimated from data for the systems representing the faces. These two tetrahedra have been sketched in order to illustrate the nature of the effect of the oxygen pressure condition on course of liquid during fractional crystallization in a system in which the crystallizing phases are closely analogous to the anhydrous members of Bowen's discontinuous reaction series.

The base of the tetrahedron of Fig. 3 includes the triangle of Fig. 2 (c), and the circle on the base corresponds with the circle HB of that triangle. The fractional crystallization of a liquid whose composition is represented by a point in the region of this circle has already been considered. Now let us move our starting liquid composition from the circle on the base up into the tetrahedron along a line extending toward the top apex, CaSiO<sub>3</sub>. Let us move it to X. This haplobasaltic liquid X on extreme fractionation will move to the right, doing so along a very



complex path which will pass through or near the points R and P, approaching finally the composition of S, a point in the right face.<sup>1</sup> In fractional crystallization the succession of crystalline phases that form as the composition of the liquid changes from X to S, although complex in detail and varying with changes in the precise composition of X, will be, in general, as follows: magnesian olivine, pigeonitic pyroxene, pigeonitic pyroxene plus iron-olivine,<sup>2</sup> diopsidic pyroxene plus iron-olivine, diopsidic pyroxene plus iron-olivine plus silica, iron-olivine plus iron-wollastonite<sup>2</sup> plus silica.

As the liquid composition moves during fractional crystallization from X toward S, liquids high in iron oxide are formed, and the greater the degree of fractionation the higher in iron oxide content the liquid will be. Olivine, pyroxenes and wollastonite also become increasingly enriched in iron oxide as the crystallization proceeds. The increase in iron content of the liquid is accompanied by a decrease in the silica content.<sup>3</sup> The effect of fractional crystallization of a haplobasaltic composition in this tetrahedron is to produce successively more iron-rich, gabbro-like crystalline aggregates.

Contrasted with this course of fractional crystallization as outlined for Fig. 3 is that for Fig. 4 where the oxygen pressure is much higher and is held constant. Magnetite has a large primary phase volume in Fig. 4. The presence of this magnetite volume prevents a liquid on crystallization from moving to high iron oxide contents.<sup>4</sup> A haplobasaltic liquid X

<sup>1</sup> The complexities and possible variations in the path of the liquid as a function of initial composition are far too great to discuss here. A study of the treatment of crystallization in the system represented by the base of this tetrahedron (Bowen and Schairer, 1935) is a good introduction to the subject. Some general relations, however, should be pointed out. The pigeonitic pyroxene and the diopsidic pyroxene that can coexist in equilibrium with the liquid represented by any point in the surface *rpR* separating the liquidus volumes of these two phases probably form a reaction pair. This is assumed to be true because when these two pyroxenes coexist in equilibrium with the liquid represented by any point on the boundary curve, *rp*, removal of heat causes the pigeonitic pyroxene to dissolve and the diopsidic pyroxene to crystallize, and when the liquid has the composition represented by the point, R, if equilibrium is maintained during crystallization, pigeonitic pyroxene dissolves while diopsidic pyroxene, silica and iron-olivine crystallize. When the liquid has the composition, P, with the removal of heat and the maintenance of equilibrium, diopsidic pyroxene in turn dissolves as iron-olivine, iron-wollastonite and silica crystallize.

<sup>2</sup> The terms "iron-olivine" and "iron-wollastonite" are used here to mean, respectively, a member of  $Mg_2SiO_4$ - $Fe_2SiO_4$  solid solution series high in  $Fe_2SiO_4$ , and a member of the  $\beta$ - $CaSiO_3$ - $FeSiO_3$  solid solution series high in  $FeSiO_3$ .

<sup>3</sup> The point, S, has the composition: 45.5 FeO, 11.5 CaO, 43 SiO<sub>2</sub>.

<sup>4</sup> The constancy of the oxygen pressure for the tetrahedron of Fig. 4 is a significant factor. The different crystallization course for mixture X in Fig. 4 from that of X in Fig. 3 is caused as much by the oxygen pressure's remaining constant as by its being at

in Fig. 4 will on fractional crystallization move to the eutectic, D, when the two pyroxenes, magnetite and silica will crystallize together.<sup>1</sup> As the fractionally crystallizing liquid proceeds from X to D, crystalline phases will in general have the sequence: magnesian olivine, pigeonitic pyroxene, pigeonitic pyroxene plus magnetite, pigeonitic pyroxene plus diopsidic pyroxene plus magnetite, pigeonitic pyroxene plus diopsidic pyroxene plus magnetite plus silica.<sup>2</sup> It will be noted that in this sequence magnetite appears with pigeonitic pyroxene and continues then to precipitate until the liquid is exhausted, whereas in the previous sequence relating to Fig. 3, iron-olivine appears with pigeonitic pyroxene and similarly continues to precipitate until the liquid is exhausted. The replacement of iron-olivine by magnetite as a continuously crystallizing solid solution series appearing midway in the crystallization sequence is the principal and critical difference between the two crystallization paths. Significantly also, the oxygen content of mixture X during crystallization remains constant in Fig. 3, but increases in Fig. 4.

Fractional crystallization of liquid X in Fig. 4 does not cause the liquid to move to high iron oxide contents, but rather the liquid assumes only a moderate iron oxide content before magnetite begins to crystallize, and after that iron oxide in the liquid decreases as silica increases. Point D has an SiO<sub>2</sub> content of about 60%.

Crystallization ceases at point D of Fig. 4, but in a natural magma significant amounts of water would no doubt be present where oxygen pressures are high.<sup>3</sup> With water present, as well as alumina and alkalis, amphibole may crystallize at about the temperature of the stage of two pyroxenes plus magnetite plus silica (point D), to be followed at a

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an initially higher level. Maintaining the oxygen pressure at a constant level during fractional crystallization causes mixture X of Fig. 4 to increase in oxygen content, and thereby causes magnetite to be quantitatively a very important phase separating. If the oxygen content of mixture X of Fig. 4 were held constant, rather than oxygen pressure, phase relations in the tetrahedron and therefore the course of crystallization would be quite different (Osborn, 1959).

<sup>1</sup> The relation between the two pyroxenes along the pyroxene surface, rpDR, can only be surmized at present. When the liquid composition is near rp there is a reaction relation. Pigeonitic pyroxene dissolves as diopsidic pyroxene crystallizes. When the liquid is at or near D, however, the magnesium content of the diopsidic pyroxene probably is reduced to the point that the two pyroxenes crystallize together.

<sup>2</sup> Alternately, magnetite might appear either before pigeonitic pyroxene or after diopsidic pyroxene, depending on precise composition of initial liquid and on degree of fractionation.

<sup>3</sup> The oxygen pressure resulting from the equilibrium,  $2\text{H}_2\text{O} \rightleftharpoons 2\text{H}_2 + \text{O}_2$ , increases with water pressure. For example, according to estimations by Kennedy (1948), at 1000° C. oxygen pressures from this dissociation increase from  $9 \times 10^{-6}$  to  $9 \times 10^{-4}$  as water pressure is increased from 1 to 1000 atmospheres.

lower temperature by biotite. Because of the relatively low silica content of amphibole and biotite, the direction of movement of the liquid toward higher silica contents continues.

TWO GROUPS OF REACTION SERIES

This analysis of fractional crystallization for compositions in the tetrahedra of Figs. 3 and 4, although very sketchy, may be helpful in understanding the nature of the discontinuous reaction series of basaltic magma. It was evident from it that two discontinuous reaction series can be drawn up, one for each set of conditions. These series, applying directly to the experimental conditions, suggest to us where reaction relations are to be expected among the minerals of actual rocks, and what we may expect there in the way of indications of their occurrence. Thus they may, in the words of Bowen (1922), "serve as a guide and stimulus to search for facts."

In Fig. 5 are sketched two groups of reaction series. Figure 5(a) has on the left a discontinuous reaction series of natural minerals and a central line for magnetite, as suggested by the relations depicted in Fig. 4. Amphibole and biotite have been added to complete the left series. On the right is shown the continuous series of plagioclase feldspars. This arrangement is similar to Bowen's diagram (Fig. 1) with the addition of magnetite and the omission of his "spinel" and also of some details

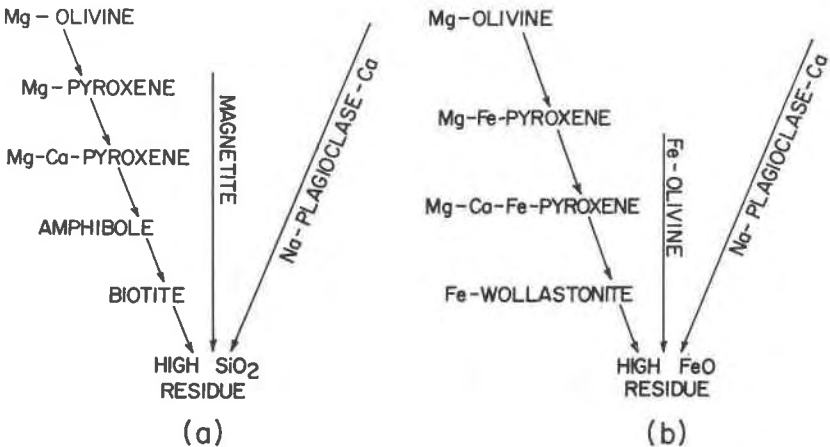


FIG. 5. Two groups of reaction series for subalkaline igneous rocks. Group (a) is related to Fig. 4 and to calc-alkaline rocks of orogenic regions. Group (b) is related to Fig. 3 and to gabbroic layered intrusions. The vertical line for magnetite and that for Fe-olivine signify continued precipitation over the length of the line, just as does the line for plagioclase.

in the low temperature part. Magnetite in this scheme is not the "spinel" of Bowen, which can form by reaction of anorthite and forsterite at high temperatures, but it is an important primary phase, a solid solution series beginning to crystallize in the early to middle stages of crystallization and continuing to form throughout the crystallization. The magnetite that crystallizes from natural magma probably changes from compositions rather high in such ions as  $Ti^{4+}$ ,  $Cr^{3+}$  and  $Al^{3+}$ , toward a composition approaching pure  $Fe_3O_4$ . The relations between the pyroxene phases are complex in the system represented by the tetrahedron of Fig. 4, and are even more so in basaltic and related magmas. In Fig. 5(a) as well as in 5(b), only an indication of trend is intended. As a basaltic magma fractionally crystallizes according to the scheme of 5(a), increase in iron oxide content of the liquid is prevented by separation of magnetite, as  $Fe^{2+}$  in the liquid is oxidized to  $Fe^{3+}$ . Increase in silica content results from crystallization of the minerals of each of the three series. The series of 5(a) are considered applicable to fractionally crystallizing basaltic magma having a significant water content. The successive liquids developing are the calc-alkaline series of orogenic belts.

In Fig. 5(b) are three reaction series of minerals forming a scheme appropriate to a fractionally crystallizing basalt under oxygen pressure conditions similar to those for Fig. 3. In this scheme magnetite is not a major phase. In its place is iron-olivine which, unlike magnetite, takes silica out of solution as it precipitates. The lower members of the discontinuous reactions series of Fig. 5(b) are at any stage richer in silica than is the liquid, and hence their precipitation tends to drive the liquid composition toward lower silica contents. The result of crystal fractionation in this scheme of 5(b) is a high FeO residual liquid. The reactions are considered to be those of basaltic magma containing very little water. Successive magmas remain basaltic or gabbroic in nature, without formation of andesitic or dioritic types.

#### TWO GROUPS OF ROCK SERIES

Liquids in the two schemes of Fig. 5 have the distinctive trends of increase in silica for (a) and increase in iron oxide for (b). Rock series originating principally by fractional crystallization according to these schemes should show these trends in successive liquid fractions. Magma series which develop might then be grouped by a simple plot of silica versus iron oxide. In Fig. 6 there is such a plot. These igneous rock series fall into two groups, those in which the liquid increases in silica as differentiation proceeds, and those in which there is an increase in iron oxide. Starting with a basaltic composition, one develops into the

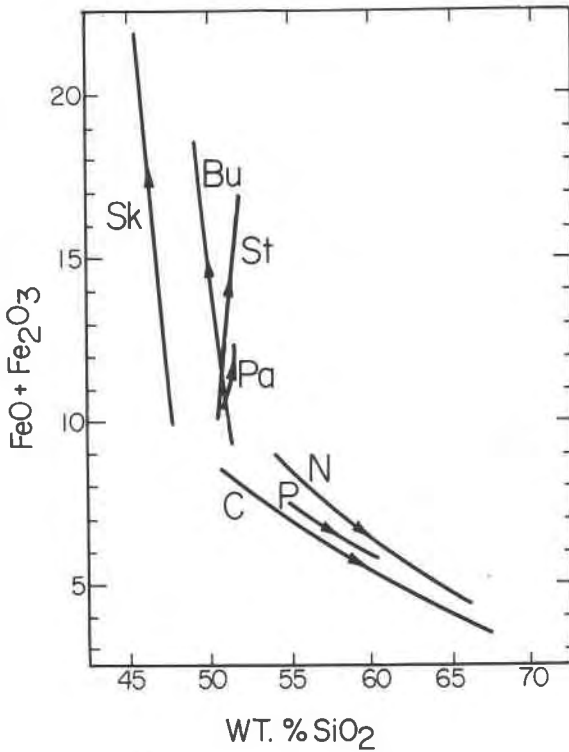


FIG. 6. Two groups of rock series. Sk=Skaergaard liquids, Bu=Bushveld, St=Stillwater, Pa=Palisade diabase, N=Nockolds' averages, P=Paricutin lavas, C=Cascades series.

calc-alkaline series of the orogens, the other into series characteristic of layered intrusions.

In Fig. 6 the calc-alkaline series is represented by three curves, labeled N, C and P. The first is derived from Nockolds' (1954) averages for the three rock types: andesite, dacite plus dacite-obsidian, and rhyodacite plus rhyodacite-obsidian. Curve C is a plot of analyses of representative volcanic rocks of the Cascades as listed by Turner and Verhoogen (1960). Curve P is a plot of analyses of lavas extruded from Paricutin volcano (Wilcox, 1954), where eruption was continued from 1943 to 1952, with the trend in change of composition as shown. The curves are very similar, iron oxide decreasing one and a half to two percent for each five percent increase in silica. The trend of the curves is certainly that to be expected of a rock series originating from basalt and

differentiating by fractional crystallization according to a reaction series scheme of the nature of that shown as Fig. 5(a). Presumably therefore the oxygen pressure remained at a sufficiently high level that significant precipitation of magnetite occurred.

Evidence is meager on the quantitative aspects of magnetite separation in basaltic and andesitic magmas of the calc-alkaline series. Wilcox (1954) was confronted with the question of magnetite separation in his analysis of the relative importance of fractional crystallization and assimilation at Paricutin. He concluded that fractional crystallization might be the explanation for the observed compositional changes of the lava series, provided that magnetite separates along with olivine and plagioclase. His objection to fractional crystallization as the "only process producing the lava suite at Paricutin volcano" lay in "the observed lack of significant amounts of movable magnetite in the rocks themselves and in view of the physical chemical arguments against such large amounts of magnetite being able to crystallize from a magma of this type" (Wilcox, 1954).

With regard to "movable magnetite" let us just say here that according to Wilcox's account magnetite was precipitating. Possibly therefore magnetite could have crystallized in significant amounts and moved by sinking. Physical chemical arguments are not opposed to this if oxygen pressure remains at an appropriate level. In short, the careful analysis by Wilcox may be interpreted as being in support of the thesis that fractional crystallization is the dominant process producing the calc-alkaline rock series as exemplified by the lower curves of Fig. 6.

The upper group of curves applies to basaltic magmas forming layered intrusions. The Skaergaard liquid line (Wager and Deer, 1939) is represented by the curve labeled Sk, the Bushveld (Hess, 1960) by Bu, the Stillwater (Hess, 1960) by St, and the Palisade diabase (Walker, 1940) by Pa. In all of these series, the trend is toward higher iron oxide without notable increase in silica. Extensive studies of the four rock series plotted in the upper curves of Fig. 6 led various investigators to the conclusion that fractional crystallization was in all cases the cause of the differentiation. Reaction series applicable would seem to be those of (b) in Fig. 5.

#### CONCLUSION

The plotting of experimental data for lime-magnesia-iron oxide-silicate systems in two tetrahedra representing very different oxygen pressure conditions leads to two different reaction series among the ferromagnesian phases. This in turn leads to the two different groups of reaction series among minerals as shown in Fig. 5. Where fractional

crystallization of basaltic magma has produced an iron-rich residual liquid, notably on the Skaergaard Peninsula in East Greenland, the observed mineral relations indicate a scheme similar to that of (b) in Fig. 5. A scheme of the type shown in (a) of Fig. 5 may have been effective in producing the calc-alkaline series of magmas, as Bowen thought. From experimental work, which is still very meager, we would judge that maintenance of a fairly high oxygen pressure, perhaps about  $10^{-7}$  atm., is the critical factor for the existence of the reaction scheme of Fig. 5(a). Experimental work to determine oxygen pressure relations of the calc-alkaline rocks at time of crystallization, coupled with petrographic, chemical and structural studies of the minerals, especially pyroxene and magnetite, may be expected to lead to a much better understanding of the role of fractional crystallization in the formation of the calc-alkaline magmas of the orogens.

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