

THE
JOURNAL OF GEOLOGY

April-May 1922

THE REACTION PRINCIPLE IN PETROGENESIS

N. L. BOWEN

Geophysical Laboratory, Carnegie Institution of Washington

INTRODUCTION

It is now many years since petrologists first began to think of the crystallization of a molten magma in terms of the physico-chemical principles governing the behavior of solutions. In the study of ordinary solutions a condition frequently found was that known as the eutectic relation. In the simple case of two components, each lowered the melting-point of the other to the temperature of the eutectic point, at which temperature both solids separated side by side from a solution of fixed composition, the eutectic mixture. This case and the analogous condition in systems of more components are now so familiar to petrologists that they need not here be enlarged upon. The concept of the eutectic was early seized upon by petrologists and has been one of great utility in petrogenic theory. It accounted for the low melting temperatures of mixtures of minerals that are individually highly refractory. It threw light on some of the factors governing the separation of minerals from their mutual solution. But most of all, it stimulated the tendency to think of magmas in the light of the laws of solutions, or, better, of phase equilibrium, and encouraged experimental research whose expected result was the location of the composition of the eutectics for chosen mineral

mixtures. In investigation of this kind, both on its theoretical and experimental sides, Vogt took a leading part and the importance of his pioneer work cannot be overestimated.

As might have been anticipated, it was soon found that the eutectic relation did not always obtain, for, after all, it is but one of many possible relations between two or more components in any system. Very early it was realized that the existence of solid solution between two components might eliminate the eutectic relation between them. Later, as more accurate methods of experimentation were introduced, examples of incongruent melting were found, which again lead to the elimination of the eutectic. Indeed, it seems that relations between the components such that the eutectic disappears are so common in mineral systems that it may be doubted whether considerations based upon the doctrine of eutexia can longer be regarded as of any great service to petrogenic theory, in spite of their great suggestive utility in the past.

It should be realized that these non-eutectic relations should not be termed anomalies nor even apparent anomalies. They are just as definitely the result of the laws of solution as are eutectics.

This paper has been written with the object of readjusting the emphasis in our conception of mineral relations. It will be pointed out that another relation between the phases, here called the reaction relation, is very common in silicates, and is at the same time a very much broader concept, with which to approach the study of petrogenesis, than the simple doctrine of eutexia, so that it might well be set up as a principle to serve as a guide and stimulus to the search for facts.

OF CONTINUOUS REACTION SERIES

The reaction relation in a common form is illustrated by the case of the plagioclase feldspars. The equilibrium diagram of the plagioclases (Fig. 1) is of a simple and familiar type.¹ Those features of it that require emphasis in the present connection may be brought out very briefly. The crystallization of any random liquid, say Ab_1An_1 , takes place in the following manner. At 1450° crystals of the composition Ab_1An_4 begin to separate. As the

¹ N. L. Bowen, *American Journal of Science*, Vol. XXXV (1913), p. 583.

temperature falls the amount of crystalline matter increases and at the same time changes in composition along the solidus curve. Thus at 1370° the crystals have the composition Ab_1An_2 . In other words, the first-formed crystals have suffered a change of composition; indeed, they are continually modified in composition by *reaction* with the liquid. Crystals and liquid mutually influence each other throughout the course of crystallization.

All of this is now an old story and is repeated here merely to emphasize the marked difference in crystallization between a mixture in such a system and one in a eutectic system. In this latter, a crystal once separated is no longer concerned in the equilibrium, which makes it in every respect a special case whose

occurrence might be expected to be comparatively infrequent, particularly in more complicated solutions (magmas).

On account of the continual reaction relation between crystals and liquid in a solid solution series such as the plagioclases, it is proposed, for the purposes of the present paper, to call such solid solutions a *continuous reaction series*. The term will apply to any solid solution series, whether to a complete series such as the plagioclases or to each separate series in the case of incomplete solid solution.

The essential feature of a reaction series, the reaction relation of crystals and liquid, is retained when the series becomes a part of a more complex system. This is true even when the end members of the series bear a eutectic relation to the newly added component, as is well shown when diopside is added to plagioclase. The

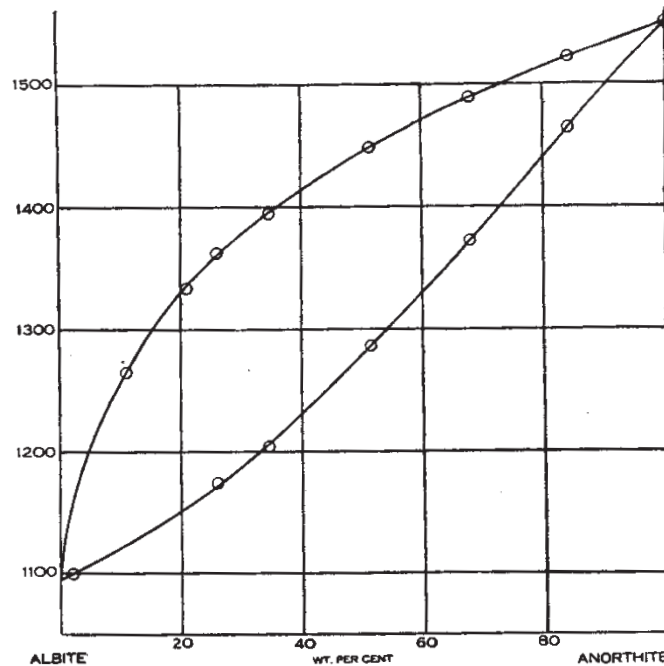


FIG. 1.—Equilibrium diagram of the plagioclase feldspars.

the liquids that are in equilibrium with two solid phases. Moreover, it lies along a valley in the fusion surface and when the object is to emphasize these features no serious objection can be raised to the term used by Vogt. On the other hand, such a usage would tend toward a non-recognition of the importance of the reaction relation between plagioclase crystals and the liquids lying along the boundary curve and, in the writer's opinion, petrology will better be served by emphasizing this relation—calling the curve, say, a reaction curve. But quite apart from the question of nomenclature, the distinction is really one of fundamental importance in petrogenesis. In the case of a true eutectic line in a ternary system, the two kinds of crystals separating bear what may be called a mere subtraction relation to the liquid and once subtracted they are no longer concerned in the equilibrium. Moreover, the true eutectic line ends in a ternary eutectic point which represents the composition that all liquids of the system must finally attain and beyond which they never pass. No such rigidity obtains in a system where the reaction relation enters. The composition of the final liquid depends upon the freedom with which reaction between crystals and liquid may take place. If the reaction is complete in the example taken, the crystals are continually made over and the last of the liquid is used up by the reaction at 1200° , when the composition of the liquid is M and all the crystals have the composition Z. But if for any reason early crystals do not participate to the full in the reaction—and this may occur when zoning of crystals or sinking of crystals supervenes—the composition of the liquid may then pass beyond M and the final liquid have a composition represented by some point between M and D, with corresponding effect on the composition of the final crystals.¹

This flexibility in the behavior of the liquid is entirely the result of the reaction relation between liquid and crystals. The course of crystallization is rendered responsive to the conditions under which crystallization takes place, for removal of crystals by zoning, sinking, or otherwise is entirely dependent on these conditions. No such response is possible in a eutectic system, for,

¹ A similar effect may of course be brought about in the binary system of the plagioclases, but it was considered unnecessary to discuss it for each case separately.

whatever the conditions, the eutectic is the goal of all liquids; all attain it; none pass it; it is a "fen of stagnant waters."

OF THE REACTION PAIR AND DISCONTINUOUS REACTION SERIES

The kind of reaction relation introduced by the existence of a solid solution series is not the only kind that is of importance in crystallizing magmas. Another type of crystallization phenomenon, ordinarily to be thought of as quite distinct from solid

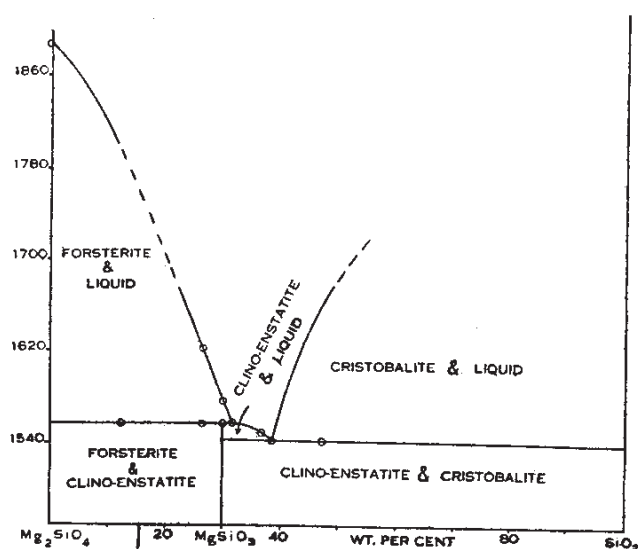


FIG. 3.—Equilibrium diagram of the system, forsterite-silica.

composition 42 per cent MgO, 58 per cent SiO₂ begins to crystallize with separation of olivine Mg₂SiO₄ and this continues until 1557° when the olivine reacts with the liquid to form the pyroxene clino-enstatite. If the opportunity for reaction¹ is perfect the liquid is completely used up by the reaction and the mass consists entirely of olivine and pyroxene. If, on the contrary, liquid and olivine are not free to continue in intimate contact for any reason, then upon completion of all reaction possible under the circumstances, some liquid will be left over. This will proceed to crystallize in the

¹ The phrase, opportunity for reaction, is used throughout this paper without explanation. It is considered that the various factors involved have been sufficiently discussed elsewhere. The removal of crystals from a part of the liquid by their sinking is a factor limiting the opportunity for reaction as far as that part of the liquid is concerned. And so it is with the formation of a reaction armor about crystals or the squeezing out of liquid from a crystal mesh. Usually the rate of cooling is the fundamental control over these factors and therefore over the opportunity for reaction.

solution, has, nevertheless, consequences of a similar nature. This type is illustrated in several systems that have been investigated experimentally, but for our present purpose we shall discuss only cases showing phases closely related to rock minerals.

The equilibrium diagram of the system MgO-SiO₂ is shown in Figure 3. A liquid of

ordinary way giving a mixture of the pyroxene MgSiO_3 and silica. We thus obtain a mass consisting of olivine, pyroxene, and silica.

Again it is found that the existence of the reaction relation introduces a flexibility such that different products are obtained with varying opportunity for reaction. Under certain conditions no free silica is formed; under others a little may be formed; and under still others a considerable amount may appear. The compound Mg_2SiO_4 and MgSiO_3 may be called a *reaction pair*. By this is meant that crystals of the first compound react with the liquid to produce the second during the normal course of crystallization.

A reaction relation of this latter type may exist between three or more compounds and the compounds, arranged in proper order, may then be said to constitute a *discontinuous reaction series*. An example of this kind of series is given by the system $\text{H}_2\text{O}-\text{K}_2\text{SiO}_3-\text{SiO}_2$ as worked out by Morey and Fenner.¹ The equilibrium diagram is given in Figure 4. A liquid of composition A begins to crystallize with separation of K_2SiO_3 . This is joined later by $\text{K}_2\text{Si}_2\text{O}_5$ and the two crystallize side by side, the liquid changing in composition along the boundary curve between their fields. At Q_1 the liquid reacts with K_2SiO_3 converting it into $\text{K}_2\text{SiO}_3 \cdot \frac{1}{2} \text{H}_2\text{O}$ and if the opportunity for reaction is perfect the whole mass solidifies. On the other hand, if the opportunity for reaction is limited, some liquid Q_1 is left in excess and it proceeds to crystallize along Q_1-Q_2 with separation of $\text{K}_2\text{Si}_2\text{O}_5$ and $\text{K}_2\text{SiO}_3 \cdot \frac{1}{2} \text{H}_2\text{O}$. At Q_2 the crystals of $\text{K}_2\text{Si}_2\text{O}_5$ react with the liquid to produce $\text{K}_2\text{Si}_2\text{O}_5 \cdot \text{H}_2\text{O}$ and solidification is complete if there is complete freedom of reaction. Here again there may be some liquid (Q_2) left over if reaction is for any reason limited and it will proceed to crystallize along Q_2-Q_3 with separation of $\text{K}_2\text{Si}_2\text{O}_5 \cdot \text{H}_2\text{O}$ and $\text{K}_2\text{SiO}_3 \cdot \frac{1}{2} \text{H}_2\text{O}$. At Q_3 the crystals of $\text{K}_2\text{SiO}_3 \cdot \frac{1}{2} \text{H}_2\text{O}$ are converted into $\text{K}_2\text{SiO}_3 \cdot \text{H}_2\text{O}$. In this case there is always some liquid in excess of that required for the reaction even with perfect opportunity for reaction, but there is more of it when the reaction is limited. The liquid then crystallizes along the boundary between the fields of $\text{K}_2\text{SiO}_3 \cdot \text{H}_2\text{O}$ and $\text{K}_2\text{Si}_2\text{O}_5 \cdot \text{H}_2\text{O}$, with separation of those compounds, until the isotherm of 200° is reached, and if there is no

¹ *Journal American Chemical Society*, Vol. XXXIX (1917), pp. 1173-1229.

further cooling some solution is left that does not crystallize at all.

It is plain from the outline of crystallization given that we have a reaction pair, $K_2Si_2O_5$ and $K_2Si_2O_5 \cdot H_2O$ and also a discontinuous reaction series, $K_2SiO_3 - K_2SiO_3 \cdot \frac{1}{2}H_2O - K_2SiO_3 \cdot H_2O$. Each member of the series is produced from the preceding member by reaction with the liquid. The series is distinct from a continuous reaction

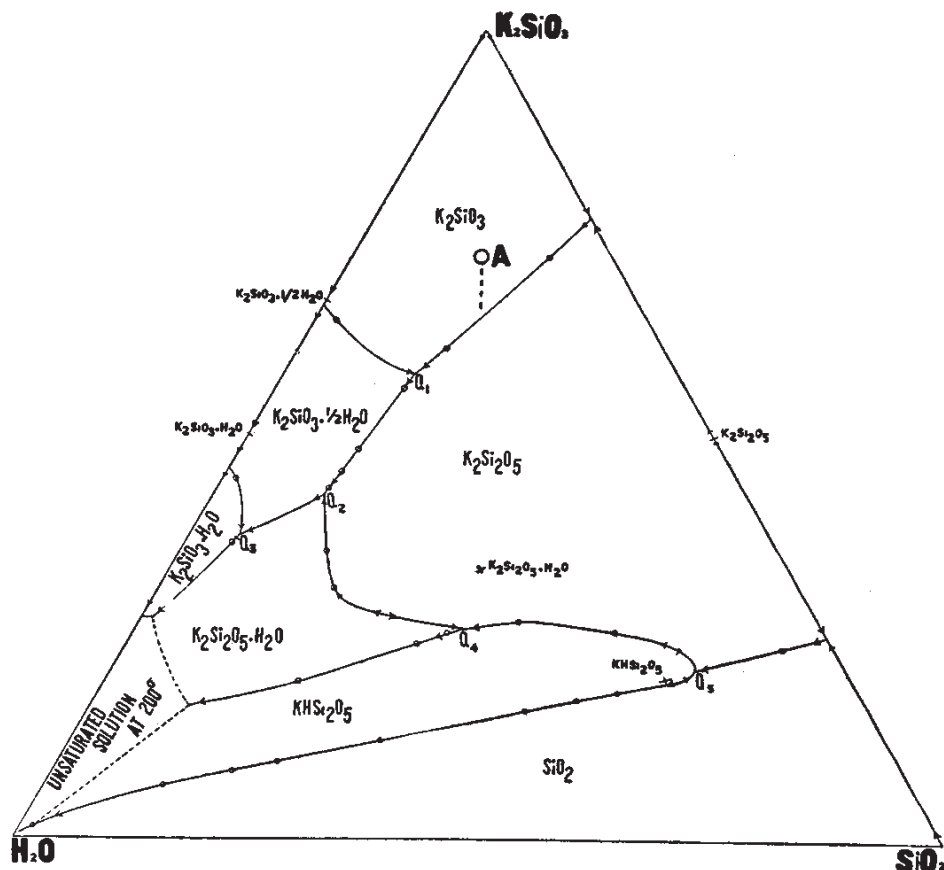


FIG. 4.—Equilibrium diagram of the system, $H_2O-K_2SiO_3-SiO_2$

series in that changes of composition are discontinuous, taking place in steps and not by insensible gradations as in the continuous series.

The consequences of the existence of this reaction series have been pointed out in the foregoing. Under certain conditions of crystallization we may get simply the three phases K_2SiO_3 , $K_2Si_2O_5$, and $K_2SiO_3 \cdot \frac{1}{2}H_2O$. Under other conditions we may get a part or all of a long chain of products including the foregoing three and in addition $K_2Si_2O_5 \cdot H_2O$ and $K_2SiO_3 \cdot H_2O$. Moreover, when crystallization runs far down in the series we may obtain a water-rich

liquid that fails to crystallize at all. The formation of this liquid under such conditions is important in connection with the abundance of analogous liquid in certain types of magma, say, the granitic.

RELEASED MINERALS

A feature of reaction series that is important in its consequences is the fact that a compound, which otherwise would not be formed from a given liquid at all, may, as a result of failure of complete reaction, be stored up in the liquid and appear as a mineral at some later stage. Such a mineral may be regarded as *released* because of the existence of the reaction relation and it is at the same time complementary in composition to the mineral disappearing during reaction. Thus in the case of the reaction pair Mg_2SiO_4 - $MgSiO_3$, free silica is released as a result of failure of complete reaction and it is complementary to Mg_2SiO_4 .

THE EFFECT OF THE REACTION SERIES ON THE ORDER OF SEPARATION

We have now examined several examples of the manner in which reaction series may render the course of crystallization responsive to external conditions. In another important particular the existence of the reaction series, continuous and discontinuous, causes the process of crystallization to depart from that obtaining in the eutectic system. In the crystallization of the plagioclase feldspars a plagioclase always separates before any other plagioclase that is less calcic. There is no such thing as the separation of calcic plagioclase first from mixtures rich in calcic plagioclase and of sodic plagioclase first (followed by calcic plagioclase) from mixtures rich in sodic plagioclase, as there would be in the eutectic system. And so with the reaction pair and the discontinuous reaction series the higher member of the series always separates before the lower, if at all. We do not have a condition in mixtures of forsterite and clinoenstatite such that forsterite separates first from mixtures rich in forsterite and clinoenstatite first in mixtures rich in clinoenstatite as there would be in eutectic mixtures. On the contrary, forsterite, however small in amount, always separates first.

Thus the existence of reaction series tends to introduce a fixity in the order of crystallization, calcic plagioclase before sodic plagioclase, if at all; forsterite (olivine) before clinoenstatite (pyroxene), if at all; K_2SiO_3 before $K_2SiO_3 \cdot \frac{1}{2}H_2O$ before $K_2SiO_3 \cdot H_2O$.

SERIES WITHIN SERIES

Both the continuous and discontinuous types of reaction series may be much more complicated than the simple examples chosen for illustration. The continuous reaction series may embrace more than two components, and the reaction between liquid and crystals will then be concerned with the adjustment of the relative concentrations of all of the components. Likewise the discontinuous reaction series may consist of any number of members. More than this, any member of a discontinuous reaction series may itself be a continuous reaction series. This case is exemplified by the system diopside-forsterite-silica.¹ Here we have the discontinuous reaction series olivine-clinopyroxene-silica in which the member clinopyroxene is itself a continuous reaction series, that is, a solid solution series. The crystallization of a liquid of this system will illustrate the complexity to which the reaction relation may lead even in this comparatively simple system. The liquid D (Fig. 5) begins to crystallize with separation of the olivine, forsterite. At K the olivine crystals begin to react with the liquid to form clinopyroxene of the composition L, and as the temperature falls the liquid reacts, not only with the remaining olivine crystals to make them into pyroxene, but also with the pyroxene crystals already present to make them more calcic. Thus at F the olivine has been completely changed to pyroxene all of which now has the composition R. In this case, too, lack of opportunity for complete reaction will have an important effect upon the course of the liquid and the kind of crystals produced from it. Failure of reaction will enrich the liquid not only in silica but also in the more calcic pyroxenes.

CRYSTALLIZATION SERIES IN ROCKS

A sufficient number of examples of the reaction relation have been given to illustrate the more important aspects of it. More-

¹ N. L. Bowen, *Amer Jour. Sci.*, Vol. XXXVIII (1914), p. 207.

over the examples have in most cases dealt with members of common rock-forming groups and the prevalence of reaction series of one kind or the other among the rock-forming silicates is indicated by these few examples. The data are not at hand—and are not likely to be for some time—for a quantitative discussion of reaction

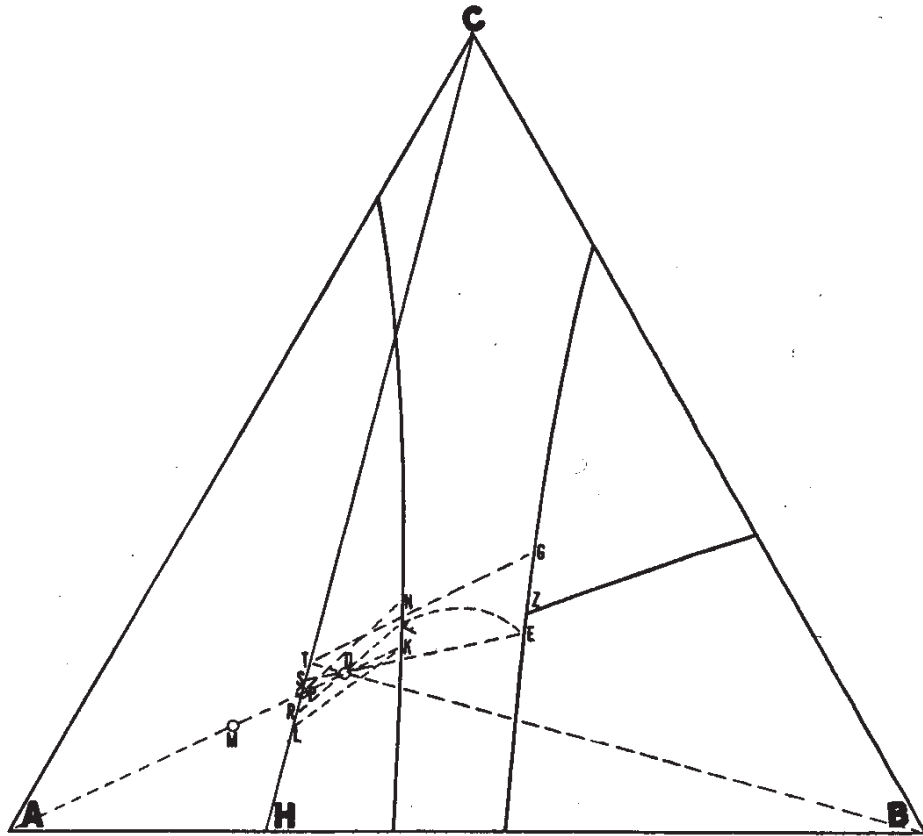


FIG. 5.—Crystallization diagram of the system, diopside-forsterite-silica. *A*, forsterite; *B*, silica; *C*, diopside; *H*, clinoenstatite, and *H-C*, clinopyroxene series.

series in mixtures corresponding to natural magmas. Nevertheless it is believed that much is to be gained from a qualitative consideration of this feature of rock-minerals.

It should be frankly stated that the existence of the reaction relation between two phases in a simple system is no guarantee of the persistence of an identical relation between them in a more complex system. In the case of the phases olivine and magnesian pyroxene, for which such a relation exists in the binary system MgO-SiO_2 , it is not unreasonable to expect that the relation might be modified in more complex systems. Actually, however, it is found that the relation persists in all the more complex systems

examined, which fact renders it more likely, but by no means certain, that the reaction relation obtains in magmatic systems.¹ The service rendered by experimental investigation, so long as it is confined to a limited number of components, must lie in its indicating where a reaction relation is to be expected. We are, moreover, instructed as to what we may expect in the way of indications of reaction and thus enabled to extend our inferences to phases not formed under laboratory conditions. This brings us to the question of the criteria of the reaction relation.

A criterion of the reaction series, common to both the continuous and discontinuous type, and serving to show their fundamental likeness, is simply the tendency of one mineral to grow around another as nucleus. In the case of the continuous series this is commonly known as zoning of mix-crystals and in the discontinuous series as the formation of reaction rims, coronas, etc. Thus we have plain evidence of this kind, from a wide range of rocks, that that the plagioclases constitute a continuous reaction series and that pyroxene, amphibole, and mica form a discontinuous series. The development of these special structures is, however, dependent on particular conditions of consolidation and the lack of such structure in an individual case should not be regarded as indicating a lack of the reaction relation in that case. It must be, in part, from a general survey of mineral relations in igneous rocks that the reaction series are deduced.

Fortunately the continuous reaction series are easily picked out, for the mere existence of solid solution or variability of composition in a crystal phase is sufficient to establish that phase as a continuous reaction series. Their number is legion, all the important igneous rock minerals with the single exception of quartz being members of solid solution series. The detection of the discontinuous reaction series is not always so easy, and the element of judgment enters to some extent.

As an example of the information to be obtained on this point from a general survey of an igneous sequence let us reproduce a

¹ Vogt believes there is no reaction relation but a eutectic relation at higher pressures between olivine and pyroxene. *Jour. Geol.*, Vol. XXIX (1921), p. 528.

table given by Harker showing the mineral relations in the sequence at Garabal Hill.¹

TABLE I
MINERAL AND ROCK SEQUENCE AT GARABAL HILL (AFTER HARKER)

	1. Iron Ore	2. Olivine	3. Augite (diplage)	4. Brown Hornblende	5. Green Hornblende	6. Biotite	7. Plagioclase	8. Orthoclase	9. Quartz
A. Olivine-diaplage-rock	+	+	+	+	-	-	-	-	-
B. Biotite-diorite	+	-	-	-	+	+	+	-	-
C. Hornblende-biotite-granite	+	-	-	-	+	+	+	+	+
D. Porphyritic biotite-granite	+	-	-	-	-	+	+	+	+
E. Eurite vein	+	-	-	-	-	-	+	+	+

It will be noted that the minerals *appear* in a certain order, as they might in a system where simple eutectic relations prevailed, but they also *disappear* in a similar order, a feature that is altogether foreign to a eutectic system. In a eutectic system no mineral ever disappears.² The first-formed mineral is simply joined by another, the pair by a third, and so on until all the minerals appear together in a final eutectic product. Very different from this is the condition actually found, namely, the disappearance of minerals in the order in which they appear which is of the very essence of the reaction series.

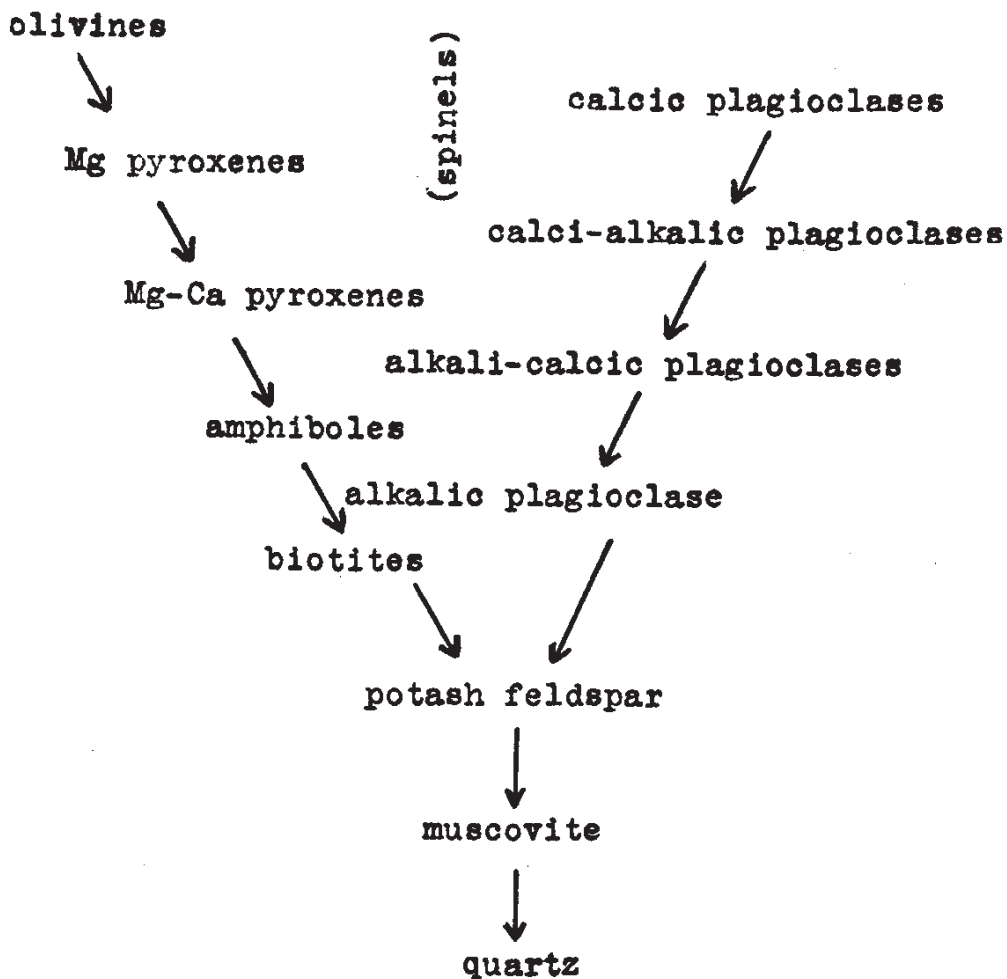
Upon examination in detail it is found that 2, 3, and 4 disappear in B, 5 disappears in D, and 6 in E. From this we conclude that these phases bear a reaction (not a mere subtraction) relation to the liquid and that, as a result of the reactions, phases appearing later are formed. We arrive at the definite conclusion that 4, 5, and 6 constitute a reaction series and at the same time note indications that they are but a part of a series containing more members.

¹ *The Natural History of Igneous Rocks*, 1909, p. 131.

² A case of simple inversion without change of composition would require to be excluded from this statement, but it has no importance in rocks at any rate.

By piecing together the information to be obtained from the examination of such sequences and observation of the structural relations of the minerals a conclusion as to the reaction series in rocks is to be arrived at. Without going into detail as to the evidence, an attempt is made below to arrange the minerals of the ordinary subalkaline rocks as reaction series. 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.

TABLE II
REACTION SERIES IN SUB-ALKALINE ROCKS



Beginning at the upper end of the series in the more basic mixtures we have at first two distinct reaction series, the continuous series of the plagioclases and the discontinuous series, olivines-pyroxenes-amphiboles, etc. As we descend in these series, how-

ever, they become less distinct, in the aluminous pyroxenes and amphiboles a certain amount of interlocking begins and they finally merge into a single series.¹ This is expressed diagrammatically by a convergence of the series, with a dovetailing of the mineral names at first, and finally a joining of the two series by the arrows converging upon potash feldspar. Just where the two series merge completely is more or less a question, but it is given closely enough for our present purpose in the figure.

That the series, olivines-pyroxenes-amphiboles-biotites, constitutes a reaction series is well attested in many rock varieties. By this is meant that liquid reacts with olivines to produce pyroxenes, with pyroxenes to produce amphiboles, and with amphiboles to produce biotites. In the continually increasing water content of the series it is related to the series K_2SiO_3 - $K_2SiO_3 \cdot \frac{1}{2}H_2O$ - $K_2SiO_3 \cdot H_2O$. The continuous reaction series of the plagioclases is perhaps the best understood series of rock minerals. This is fortunate, for the series happens to be of particular importance in that it runs through a wide range of conditions and compositions in the rock series. We simply have a continual enrichment of the liquid in alkaline feldspar with the separation of the potash variety of alkaline feldspar as a separate phase when it has exceeded its solubility in the plagioclase mixture. With the formation of potash feldspar in the one series and of biotite in the other, the two series are now so intimately intermingled as to constitute a single series.

There is a little of the nature of eutectic crystallization in the crystallization series given in the foregoing. At early stages and as between the two series there is some suggestion of the eutectic relation in that a member of one series lowers the melting "point" of a member of the other series. Moreover the one or the other begins to separate first according to which is present in excess over certain fixed proportions. There the analogy with eutectic crystallization ends for the simple reason that there is no eutectic, no inevitable end-point where final solidification must take place when the liquid has attained a certain composition. The minerals

¹ The two series are bridged at the very outset by spinel but this has, on the whole, no great practical importance.

have a reaction relation to the liquid, not a mere subtraction relation. Each separated mineral tends always to change into a later member of the reaction series. This change of composition is effected by reaction with the liquid, and according to the opportunity for reaction the liquid is entirely used up, in some cases sooner, in others later, and only then is solidification complete.

Thus we see that rock series cannot be partitioned off into such divisions as gabbro, diorite, etc., each having a eutectic of its own. All of these belong to a single crystallization series, to a single polycomponent system, which is dominated by reaction series.

Even after what is ordinarily termed complete consolidation of the rock many changes of a reaction nature may occur between the minerals. Usually a small amount of liquid is a factor in these changes which are commonly described under the head, metamorphism. Certain aspects of these changes have been described by V. M. Goldschmidt in a paper on metasomatism.¹ It is important to note in the present connection that metasomatic reactions are not confined to the metamorphic stage but are, as we have seen, a constant feature of the whole process of crystallization of the magma. Eskola has presented evidence for believing that, at times, the original crystallization of a magma may itself take place under the conditions that are ordinarily prevalent during metamorphism. The rock then presents a "mineral facies" identical with that of a metamorphic rock of the same composition formed under the same conditions. Totally different reaction series would be concerned in the crystallization of these rocks and we have not gone far toward an understanding of these, though Eskola has done much to set us on our way.² The variation of conditions necessary to produce different facies is of a different order of magnitude from the variation of conditions here considered. This is largely a variation of the rate of cooling and we are here concerned mainly with the diverse rocks in the common and definitely established sequence that can be produced under the conditions of his diabase facies principally. With adequate

¹ *Economic Geology*, Vol. XVII (1922), p. 105.

² P. Eskola, *Norsk Geologisk Tidsskrift*, Vol. VI (1920), pp. 143-94.

fractionation under conditions of slow cooling we may, however, have such concentration of mineralizers and consequent lowering of consolidation temperatures that conditions correspond to those of other facies.

EMPIRICAL RULES REGARDING ORDER OF CRYSTALLIZATION

As the result of a most extensive knowledge of the relations of minerals in rocks Rosenbusch formulated certain rules regarding the order of crystallization. When petrologists began to think of the crystallization of rocks in terms of eutectics these rules seemed to be quite at variance with theory, for this stated that those minerals should separate first that were in excess over eutectic proportions. To reconcile this with Rosenbusch's rules giving a fixed order of crystallization was a very difficult problem, and yet it was conceded that his rules represented the facts in very remarkable degree. In the light of the reaction principle no such difficulty is encountered. It is characteristic of the reaction series, as we have already seen, that however small an amount of any member may form, it always forms before a lower member of the series. In so far as reaction series control the crystallization of rocks they tend to produce a fixed order of crystallization.

Another generalization concerning the order of crystallization came from the French school of petrology. It was that the minerals separate in the order of their fusibilities, the least fusible first. This generalization, too, in the light of the doctrine of eutectics seemed to be quite absurd, but here again there is a very considerable accord with the facts. Such substances as spinel and chromite are among the most refractory materials known. Magnesian olivine has the highest melting-point of the common rock-forming silicates. The more magnesian pyroxenes stand next in the list, with the more calcic feldspars about on a par with them. The more complex pyroxenes, the amphiboles, and in particular the more alkalic feldspars are lower still. And this list corresponds very satisfactorily with the order of separation of the minerals from magmas. Again we are dealing with a tendency that is introduced by the presence of reaction series. It is a familiar character of a reaction series of the continuous type that the higher melting

members should crystallize first (witness the plagioclases), and there is a no less distinct tendency in this direction in the discontinuous reaction series.

This explanation and vindication of the doctrine of the French school is not, however, to be regarded as a proposal that we should reverse the attitude arising from eutectic considerations and accept unreservedly the statement that minerals separate in the reverse order of their fusibilities. There are too many obvious exceptions to such a rule. However, these exceptions are themselves such as might be anticipated in a system dominated by reaction series. We have seen on an earlier page that certain minerals that may be called released minerals may appear in such a system. It is apparently minerals that belong in this category that constitute the more notable exceptions. The principal of these is quartz. It is a released mineral of the reaction, olivine-pyroxene and no doubt has a similar relation in the reaction, potash feldspar-mica, a sort of hydrolysis requiring an adequate concentration of water. It is a mineral of high melting-point but separates very late—a fact that is to be connected with its character as a released mineral. In other words, it may be regarded as not actually present in the liquid at an early stage, but as released later in consequence of the reactions mentioned.

Some minerals may separate early when intrinsically present and may also appear as released minerals at later stages. Magnetite is a particularly good example. It may separate very early from a gabbro and it may be formed very late as a result of, say, the pyroxene-hornblende reaction and in particular of the mica-feldspar reaction.

PROGRESS TOWARD AN UNDERSTANDING OF REACTION SERIES IN MAGMAS

At this place it may be well to point out where we are in particular need of increased knowledge in order to understand the exact nature of the reactions occurring. It will be noted that each member of the discontinuous reaction series, olivines-pyroxenes-amphiboles-biotites, is itself a continuous reaction series. Of the olivines and the pyroxenes we know a fair amount, but practically

nothing is known as to the details of the amphiboles or the biotites as reaction series, and this means not merely their possible range of composition but also how those compositions are arranged in the series. The continuous reaction series of the plagioclases occupies a more conspicuous place than the other continuous reaction series, not merely because we know more about it, but because, as already pointed out, it enters into the rock series through a much wider range of conditions. Of the plagioclases we require to know how the potash feldspar enters into their make-up and, in the present connection particularly, at what stage in its concentration the potash molecule must appear as a separate phase. We require to know, too, the exact composition of pyroxene that forms by reaction from olivine of a certain composition, the exact composition of amphibole that forms from a certain pyroxene, and so on. These are questions on which much light may be shed by systematic equilibrium studies in synthetic minerals and by careful separation and analysis of associated minerals in various rock types. Studies of this kind are now being carried on at this Laboratory by Aurousseau on olivines, by Washington and Merwin on pyroxenes, and by Buddington on melilites. Eskola points out the importance of such work on the natural minerals, referring to it under the special name, *facies petrology*.¹ The results of these and kindred investigations may be profitably regarded in the light of their bearing on the reaction principle, for in their manifold details they are likely to prove excessively wearisome unless considered in relation to some such co-ordinating principle.

REACTION SERIES AND MAGMATIC DIFFERENTIATION

As the information gained from such studies of reaction series accumulates, our knowledge of igneous rock differentiation should increase conspicuously, for the reaction principle is the very life-principle of differentiation. We have seen, in our examination of the simple systems used to illustrate reaction series, how the existence of the reaction relation lends a flexibility to the behavior of a cooling liquid, renders it capable of giving different products

¹ P. Eskola, "The Eclogites of Norway," *Videnskapselskapets Skrifter I. Math. Naturv.*, Klasse No. 8 (1921), p. 6.

according to the conditions under which it cools. This is equally true of the complex reaction series that dominate the crystallization of magmas an outline of which, for the subalkaline magmas, is suggested in Table II. As a result of the existence of the reaction relations there indicated, it may come about that a magma precipitating olivine may, at a later stage, react with the olivine and convert it into pyroxene, and, according to the extent to which controlling conditions facilitate the reaction, the whole future course of the magma is modified. If conditions are particularly favorable the reaction may be complete and the olivine may disappear, its place being taken by pyroxene. The liquid then cools further with deposition of later members of the crystal series. If conditions are not so favorable some olivine may be left unchanged and, in consequence, a somewhat different liquid is left to pass on down the crystal sequence. So it is with the reaction, pyroxene-amphibole. Not only that, but within each mineral group the reactions may be variously facilitated under different conditions. This is true not only of the members of the olivine-pyroxene-amphibole series but also of the plagioclase series, and the liquid may be entirely used up by reaction, sometimes earlier, sometimes later. It need not be surprising, therefore, that the differentiates derived from a gabbro magma may vary both in scope and quality. We may have only gabbro and diorite in one case, but a longer sequence including granite in another. We may have a potassic granite in one case and a sodic granite in another. Rapid crystallization at an early stage, with subsequent slowing-up, seems to bind up much of the potash feldspar in the early formed plagioclase and give a sodic granite. On the other hand slow cooling throughout seems to avoid this factor and give potash granites. Too little is known as yet of the details of the various reaction series to make possible any very definite statements on these points.

In offering an outline of crystallization series in rocks (and therefore of differentiation) the list has been carried only as far as the constituents of granite. This should not be interpreted as indicating that there is anything final about the granite with respect to differentiation series. We have seen in the system K_2SiO_3 - SiO_2 - H_2O that when any mass is cooled to 200° and no farther there will commonly be a liquid left over that never crystallizes.

The composition of this liquid lies at some point on the 200° isotherm. If the cooling were continued to 100° and no farther there would again be liquid left whose composition would be represented by a point on the 100° isotherm, and this liquid would never crystallize. And so it would be for any temperature except some negative temperature at which the water itself would appear as ice.

A similar condition will prevail in the aqueous system represented by magmas. The cooling of rocks is always limited by the temperature of their surroundings. There is always a liquid left that does not crystallize and it is probable that to the very last the rock constituents bear a reaction relation to this liquid.

In this connection the behavior of liquids crystallizing along the boundary Q_5 - H_2O (Fig. 4) may be instructive. At the higher temperatures crystallization consists of the simple separation of both $KHSi_2O_5$ and quartz, but at lower temperatures $KHSi_2O_5$ separates and quartz redissolves, or, better, the liquid reacts with quartz, converting it into $KHSi_2O_5$. If the reaction is not free to take place the liquid leaves the boundary curve, passes into the $KHSi_2O_5$ field, and thereafter only $KHSi_2O_5$ separates from it, no quartz. Thus we have a reaction relation between liquid and crystals at the very latest stages and, in consequence of it, alternative behavior of the liquid.

There are some indications that in granitic liquid at the pegmatite stage, more or less similar conditions prevail. Quartz may react with liquid to produce feldspar and sometimes the graphic structure may be a result of this reaction (replacement). Why replacement should produce graphic structure in some instances and not in others is not apparent, but the possibility should be considered that graphic structure may often be the result of replacement both in rock minerals and in ore minerals. The graphic intergrowth of spinel and pyroxene seen in certain rocks can scarcely be interpreted otherwise than as due to reaction.¹ Experimental work on systems involving these phases shows pretty definitely that anything suggesting a eutectic relation between spinel and pyroxene is not to be entertained.²

¹ W. N. Benson, *Jour. Proc. Roy. Soc. N. S. Wales*, Vol. XLIV (1910), p. 521.

² Rankin and Merwin, "The Ternary System $MgO-Al_2O_3-SiO_2$," *Amer. Jour. Sci.*, Vol. XLV (1918), pp. 301-25; also Olaf Andersen, "The System: Anorthite-Forsterite-Silica," *Amer. Jour. Sci.*, Vol. XXXIX (1915), p. 437.

If a reaction of the kind suggested (involving quartz, feldspar, and mica molecules) is a definite feature of pegmatitic granite it is possible that failure of reaction may produce a liquid deficient in silica, just as such a liquid is produced in the system above. From this liquid feldspathoid may be deposited instead of some of the feldspar. Thus it is possible that alkalic rocks may, in some cases, be formed as a result of the reaction relation among the minerals noted. Foye has noted a very intimate relation between the granite pegmatites and nephelite syenite of Haliburton, Ontario.¹

NOTE.—Since the foregoing was written it has been demonstrated by Morey and Bowen that leucite and orthoclase constitute a reaction pair with quartz as a released mineral. The importance of the reaction principle in connection with the origin of some alkaline rocks is confirmed by these facts but the full significance cannot be discussed here.

SUMMARY

Petrogenic theory has passed beyond the stage where the conception of eutectics can longer be regarded as of any considerable service. Experimental investigations and the study of the rocks themselves, in the light of such investigations have made it clear that the eutectic relation is unimportant but that another relation between liquid and crystal phases, here called the reaction relation, is of fundamental significance. The ordinary solid solution series such as the plagioclases may be regarded as a *continuous reaction series* because during crystallization each member is produced from an earlier member by reaction with the liquid, the variation of composition being continuous. There are also *discontinuous reaction series* exhibiting related characters but with discontinuous changes of composition. The series olivine-pyroxene-amphibole-mica is a prominent example among the rock-forming minerals.

On the basis of these considerations the minerals making up the rocks of an igneous sequence can be arranged as reaction series and it is the existence of such series that controls the crystallization and differentiation of the rocks of the sequence. Even the graphic structure, usually regarded as a eutectic structure, is probably to be considered the result of reaction between the phases in many examples.

January, 1922

¹ *Amer. Jour. Sci.*, Vol. XL (1915), p. 436.