A COTECTIC-REACTION DIAGRAM FOR IGNEOUS ROCKS

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INTRODUCTION

Many features concerning the crystallization of igneous rocks may be conveniently summarized digrammatically. The diagram suggested here portrays rather simply and concisely numerous relations for the common igneous rock-forming minerals. It is not an attempt to reduce all silicate phase studies to a single representation. It is proposed as a pedagogical aid, and it should be introduced after the student has become familiar with the phase diagrams for a number of silicate systems. It should not be used as a substitute for the phase diagrams themselves. The scheme has limited value and should be used with caution. The diagram is not quantitative and it should not be employed in problem solving. It merely serves to illustrate in a general way the kinds of phases and the chemical trends in these phases during crystallization on the basis of the most diagnostic cations.

One of the most outstanding contributions to petrology in the early part of the present century was the concept of reaction series in igneous rocks (Bowen, 1922).

Brammall (1936a) was perhaps the first to point out the relationship between crystal structure and members of the reaction series. He described the plagioclase series of continuous reaction as one in which (Na^+ Si^{4+}) gradually replaces (Ca^{2+} Al^{3+}) while the initial pattern of the crystal structure persists unchanged. He considered the discontinuous reaction series of mafics as consisting of a number of abrupt changes in crystal structure occurring as steps from simple to complex with falling temperature in the following sequence: unit tetrahedron $(SiO_4)^{4-}$ ⟶ single chain $(SiO_3)^{2-}$ ⟶ double chain $(Si_4O_{11})^{6-}$ ⟶ extended sheet $(Si_4O_{10})^{4-}$.

Brammall (1936b) indicated further that in the continuous reaction series (plagioclase) aluminum is lost by the addition of silicon while in the discontinuous series (mafics) aluminum is gained by the loss of silicon. In this respect he considered the two series as reciprocally related.

Von Eckermann (1944) noted an additional reciprocal relation. The increasing volume of the unit cell in the discontinuous series is accompanied by a decreasing unit cell volume in the continuous series. He noted further that the (Na, K) : Al ratio increased from 1.0 to 3.0 in both the continuous and discontinuous series whereas the Si : Al ratio changed from ∞ to 3.0 in the discontinuous series and from 1.0 to 3.0 in the continuous series.

Whereas Bowen emphasized two independent series (mafics and plagioclase), Barth (1952) considered a third (the alkali feldspars).

COTECTIC-REACTION RELATIONS

In the present paper the principal igneous rock-forming minerals are placed in five more or less independent divisions: plagioclase feldspars, mafics, quartz, leucite-alkali feldspars, and nephelines. In a very general way these five divisions are somewhat analogous to members of a eutectic system in that the presence in a system of a potential member of one division reduces the melting or crystallizing temperature of members of another.

More properly the relation between divisions may be referred to as cotectic in nature. Cotectic (Vogt, 1929; 1931), which implies simultaneous melting (or crystallization), conveys the idea that crystallizing intervals for members of different divisions may overlap one another in time. Such overlap is not only the general rule but occurs throughout a wide range of temperature. Thus crystallization within any one division might be thought of as proceeding roughly independent of that within all others. With two principal exceptions, only one member of a mineral division is in equilibrium with the melt at any one time. One exception is found in the mafic division and the other in the alkali feldspars. Both exceptions will be considered later.

Individual divisions range widely in their crystallization behavior. Plagioclase constitutes a solid solution series in which the more calcic varieties are made over by reaction with the melt to more soda-rich types as temperature falls. The alkali feldspars and nephelines constitute similar continuous reaction series. Quartz on the other hand maintains essentially a constant composition regardless of temperature.

The mafic division is the most varied and complicated and consists of the olivine, pyroxene, amphibole, and biotite groups. Each of these four groups constitutes a solid solution series with continuous reaction from higher temperature, magnesium-rich varieties to lower-temperature, iron-rich types. Not only is there a reaction relation within each of these four groups, but there is in a general way a reaction relation between the groups as Bowen showed. He defined the mafic division as representing a discontinuous series in which, as temperature falls, olivine tends to be converted to pyroxene, pyroxene to amphibole, and amphibole to biotite.

Discontinuous reaction relations between categories of the mafic division though generally true are not always realized, however. Very commonly minerals of these groups show cotectic relations. But in spite of this each mafic group exhibits continuous reaction relations. The more complicated behavior of the mafic division is perhaps in large part due to differences in temperature, pressure, and water content of the system.

In view of the fact that there is cotectic crystallization between more or less independent mineral categories or reaction series and somewhat limited cotectic crystallization within one of the reaction series (mafics), the whole phenomenon may be conveniently referred to as cotectic-reaction crystallization.

THE COTECTIC-REACTION DIAGRAM

The relationships are presented in some detail in Figure 1. For con-

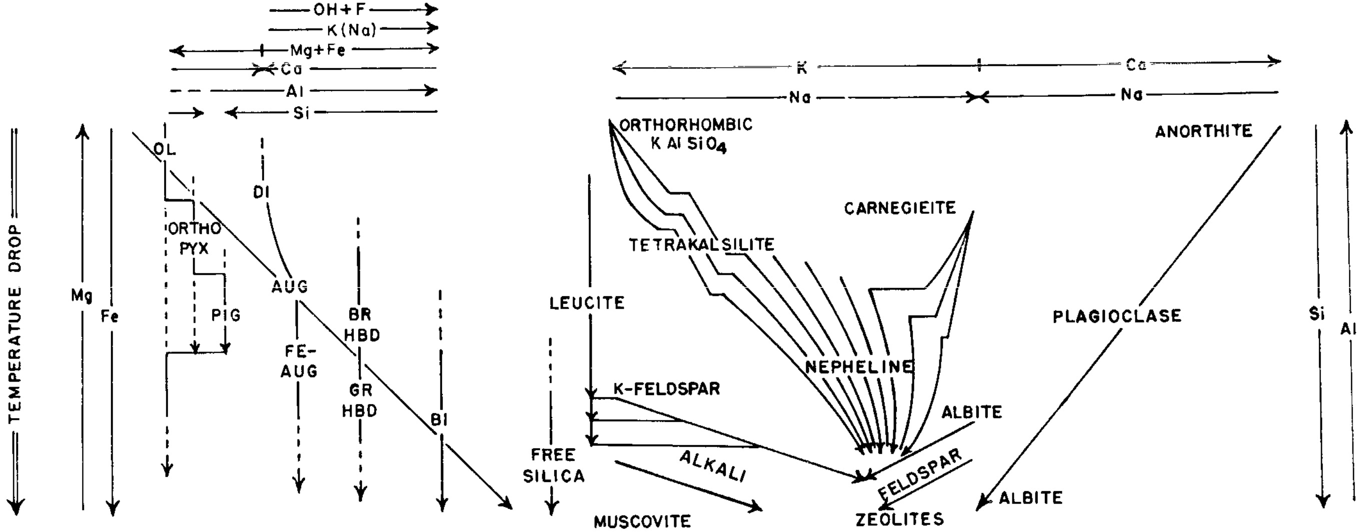

Fig. 1.—A cotectic-reaction diagram for igneous rocks. OL = olivine, ORTHO PYX = orthopyroxene, PIG = pigeonite, DI = Diopside, AUG = augite, FE-AUG = ferroaugite, BR HBD = brown hornblende, GR HBD = green hornblende, BI = biotite.

venience this figure may be divided into two parts: the felsic or tectosilicate mineral portion and the mafic or structurally simpler silicate mineral portion. The relatively simple continuous reaction series of felsics are placed to the right of quartz (free silica). The more complicated discontinuous series of mafics is shown to the left of free silica. Arrows at the top and margins of the figure indicate the direction in which enrichment in various elements occurs for each half of the diagram. Drop in temperature, which corresponds roughly with time in the case of crystallization of a melt, is indicated by an arrow, at the extreme left, which applies to the entire diagram.

Crystallization of silica takes place with falling temperature but without change in composition. Once begun crystallization may not be continuous; quartz may be resorbed as crystallization proceeds and at a lower temperature may commence to crystallize again. In other words, the composition of quartz is unaffected by the temperature and composition of the melt, but the time and temperature of quartz crystallization may be affected by the composition of the melt.

The plagioclase series is represented by an inclined arrow which shows how continuous reaction in this series leads progressively to an enrichment in Na + Si and empoverishment in Ca + Al. Crystallization might start at any point along the arrow (depending upon the chemical and physical environment) and proceed to some lower point.

The alkali feldspars are represented by two sets of converging arrows originating at K-feldspar and albite. The higher set indicates the higher temperature relations, namely continuous solid solution with a minimum (Bowen and Tuttle, 1950). These arrows express the tendency for the solid phase of a more potassic alkali feldspar system to drift toward the sodic component and for that of a sodic alkali feldspar system to become somewhat more potassic.

The lower set of opposing arrows represents conditions of crystallization at lower temperature and higher water content (Yoder, *et al.*, 1957). The wide horizontal separation of the two arrowheads corresponds to the gap in this discontinuous solid solution system where the solvus intersects the solidus. Systems falling within the gap may crystallize simultaneously the two types of feldspar whose compositions are represented by points of the arrowheads. Crystallization in the early stages of such a system will generally result in a single phase, either more sodic or more potassic. This phase will change in composition toward the corresponding arrowhead. Upon reaching the arrowhead the second phase will appear with a composition represented by the point of the other arrowhead. Henceforth both phases crystallize until the system is completely solid or until one or both are replaced by other phases. The Si and Al arrows at the right of the digram obviously do not apply to the alkali feldspar series.

Closely related to potash feldspar is leucite. This relationship is expressed by the vertical arrow which indicates a change of temperature without change in composition. At its lower end the arrow is joined to the alkali feldspar portion of the diagram by horizontal lines. These lines indicate peritectic reaction at different temperatures between leucite and potash feldspar. The slight horizontal offset of these two arrows expresses roughly a difference between leucite and potash feldspar in potash content.

The nepheline series is more complicated, and the relations shown in Figure 1 are based largely upon laboratory studies (Schairer, 1950). Melts near the potash end of the series crystallize orthorhombic (K, Na) $AlSiO_4$ which in nature is probably represented by the mineral kaliophylite or kalsilite. This phase, which represents the most potassic and highest temperature variety, becomes slightly more sodic at lower temperatures and is finally converted to a more sodic phase called tetrakalsilite (Tuttle and Smith, 1958). At lower temperatures tetrakalsilite becomes more sodic and is finally converted peritectically to a more sodic nepheline. Through continuous reaction at progressively lower temperatures, the nepheline becomes still more sodic. The three arrows originating at orthorhombic $KAlSiO_4$ indicate approximately the two limiting and one intermediate chemical trends involving these three phases. The horizontal offsets in these arrows indicate the wide range in temperature and composition over which each of the two peritectic reactions may take place.

Melts near the sodic end of the series crystallize carnegieite which reacts continuously at lower temperatures to become more potassic. Finally through peritectic reaction, carnegieite is converted to a more potassic nepheline. With further drop of temperature alkali changes in the nepheline are relatively minor. The three arrows originating at carnegieite are analogous to those originating at orthorhombic $KAlSiO_4$. The horizontal offsets, which indicate peritectic reaction, show progressively greater chemical differences between the two phases at higher conversion temperatures. Furthermore, in a system where conversion has occurred at the higher temperature, further cooling promotes sodic enrichment in the nepheline. In a system where the conversion temperature is lower, nepheline may be first enriched in soda and later in potash. In a system with a still lower conversion temperature, progressive enrichment in potash takes place.

In systems of less extreme compositions orthorhombic (K,Na) $AlSiO_4$, tetrakalsilite, and carnegieite are not stable; and nepheline of an intermediate composition may crystallize. Continuous reaction converts this nepheline to a more sodic type in most cases. These changes in alkali content are represented by the central group of shorter arrows. The diagram brings out rather strikingly the fact that although a wide range in composition of the solid phase may exist at higher temperatures there is a convergence due to reaction at progressively lower temperatures leading to a soda-rich nepheline. The arrows should continue to the base of the diagram but have been terminated above the base so as not to obscure the arrows for the alkali feldspar series. Only very roughly does the vertical shift in this series represent the slight increase in Si and decrease in Al with falling temperature.

The right-hand portion of Figure 1 brings out a general convergence on sodium in the late stages of the three felsic series.

The more complicated relations of the mafics are shown in the left part of Figure 1. The vertical arrows represent the several more or less independent continuous reaction series in each of which the Fe:Mg ratio increases with fall in temperature. These series are in large part cotectically related; hence, phases from two or more mafic series may crystallize concurrently. The inclined arrow represents the mafic division as a whole and expresses generalized changes within this division as a discontinuous reaction series. It indicates the general change in Si, Al, Mg+Fe, Ca,K,OH, and F contents as temperature drops and as successive reaction series take over. It presents very simply the features more accurately brought out by the en echelon arrangement of the vertical arrows.

A general course of crystallization in the olivine and lime-poor pyroxene series is shown by solid lines. It involves the reaction of magnesium olivine to form magnesium orthopyroxene in an early stage, the inversion of more iron-rich orthopyroxene to form pigeonite in a later stage, and the conversion of iron-rich pigeonite back to olivine (iron-rich) in the late stage. The shift from left to right and back again in these conversions corresponds to slight increase and decrease respectively in the Ca:Mg + Fe ratio and minor changes in Si and Al in these mafic minerals. These changes between olivine and lime-poor pyroxene may take place over a range of temperature and composition (Fe:Mg) or in some cases may not occur at all. The dashed lines indicate alternative courses of crystallization. Under some conditions orthopyroxene may precede olivine in crystallization or olivine and orthopyroxene may crystallize in part concurrently. The diagram illustrates the characteristic association of olivine (magnesium-rich) with ultramafic rocks and early gabbros, its absence from slightly younger rocks, and its reappearance as an iron-rich variety in ferrogabbros of large stratiform basic plutons. Olivine found in certain granites and syenites is universally iron-rich.

Calcic pyroxene may crystallize cotectically with the olivine and lime-poor pyroxene series. Although diopsidic pyroxene may commence to crystallize before olivine, it generally starts to form after olivine first appears. The slight curve in the calcic pyroxene arrow reflects principally the slight decrease in Ca:Mg + Fe ratio commonly found in this series.

The olivine and pyroxene relations considered above are based largely on the work of Bowen and Schairer (1935), Hess (1941) Poldervaart and Hess (1951) and Wager (1939).

Relatively little is known concerning the crystallizaton of amphiboles and biotites, but the general relations are indicated by two additional arrows. The dashed lower portions of the amphibole and lime-poor pyroxene arrows express a tendency for late-stage members to become enriched in sodium and ferric iron.

Commonly, however, pyroxene gives way to amphibole which in turn reacts to form biotite in the late stages.

At low temperatures and in the presence of much water the relations in igneous rocks are complicated. Many new minerals may appear, but only muscovite and zeolites are shown in the diagram.

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