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EFFECTS OF THE CHANGES IN SLOPE OCCURRING ON LIQUIDUS AND SOLIDUS PATHS IN THE SYSTEM DIOPSIDE-ANORTHITE-ALBITE[1]

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ABSTRACT

Liquidus and solidus paths in the system diopside-anorthite-albite exhibit changes in slope. When plagioclase crystallizes alone from a ternary liquid both paths are steeper than in the system anorthite-albite, but when plagioclase is joined by diopside both paths become much less step than in the binary system. This fact, together with other evidence, suggests that the liquidus profile of an igneous rock series may be characterized by three shelves (where small temperature changes cause much fusion or crystallization, and large compositional changes) separated by steep slopes (where large temperature changes cause little crystallization or fusion, and small compositional changes). The shelves extend across picritic compositions (upper), basic and intermediate compositions (middle), and acid compositions (lower). The changes in slope may help to account for the relative proportions of various igneous rocks in different petrographical associations. The origin of primary basaltic and intermediate magmas, and the rarity of intermediate rocks in basic-acid igneous associations are discussed. Marginal zoning, oscillatory zoning, and the development of two generations of crystals (with continuous cooling) are discussed in terms of changes in slope of solidus paths.

INTRODUCTION

During the fractional crystallization of basaltic magma, the composition and behavior of early precipitates of olivine, plagioclase feldspar, and pyroxene are important in determining the composition and amount of later differentiates. Concepts of basaltic differentiation have therefore been influenced by the phase diagrams for the systems forsterite-fayalite (Bowen and Schairer, 1935) and anorthite-albite (Bowen, 1913). Each system forms a complete series of solid solutions, with melting intervals at temperatures intermediate between the melting points of the end members, and the liquidus and solidus curves form simple loops with no abrupt changes in slope. This simple pattern, of course, does not persist in more complex systems. Addition of Ca_2SiO_4 to the system forsterite-fayalite produces an extensive shelf on both liquidus and solidus surfaces of the orthosilicate plane (Ricker, 1952[2]). Possible effects of this shelf, if it persists in the natural peridotite-basalt system, were discussed in an earlier paper (Wyllie, 1960; Buddington pointed out, in conversation, that the term "plateau" used in this paper to describe the gently sloping areas on the liquidus and solidus surface is inappropriate, and the term "shelf" is now adopted). Examination of Bowen's (1915) results in the system diopside-anorthite-albite reveals that addition of diopside to the system anorthite-albite produces a pattern of slopes for liquidus and solidus paths which is rather similar to that produced by addition of Ca_2SiO_4 to the system forsterite-fayalite.

LIQUIDUS AND SOLIDUS PATHS

Equilibrium and fractionation liquidus paths have frequently been discussed in geological literature, but solidus paths have received less attention. Liquidus and solidus paths illustrate the compositional changes of coexisting liquids and crystals with increase or decrease in temperature. If a path is steep, large temperature changes produce small compositional changes, whereas if a path crosses a gently sloping shelf, small changes in temperature produce large compositional changes.

In each of the binary systems forsterite-fayalite and anorthite-albite there is one liquidus path and one solidus path, and their slopes change continuously from one component to the other. In a multicomponent system there are many liquidus paths which vary with the composition of the initial liquid (crystallization processes) or crystalline mixture (fusion processes), and with the degree of fractionation. For each liquidus path there are several solidus paths giving the compositions of minerals in equilibrium with the liquids at various temperatures. With decreasing temperature the minerals may be precipitated or resorbed. An example of the latter situation is offered by the reaction relationship exhibited by olivine in many silicate systems and in some basic magmas. A discontinuity occurs in the slope of liquidus and solidus paths whenever a phase

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[2] The solidus surface must be intersected by a solvus between the forsterite-fayalite and the monticellite-kirschteinite series, and this certainly contributes to the shelf feature on the solidus, which is indicated by Ricker's preliminary data.

appears in or disappears from the system. In many systems, rather abrupt changes in slope occur with no change in the number of phases.

A certain amount of supersaturation is required to initiate crystallization of most liquids, and the amount required depends upon the properties of the liquid and crystals. A moderate degree of supersaturation in silicate magmas probably leads to the precipitation of a few crystals which attain large sizes. If crystallization is initiated at a higher degree of supersaturation the number of crystals precipitated increases markedly but they remain small (Turner and Verhoogen, 1960, p. 47). When a liquidus path is steep the liquid temperature must fall quite far below the liquidus to produce much supersaturation, but when the slope is gentle a high degree of supersaturation can be produced if the liquid temperature falls only slightly below the liquidus.

The nature of the continuous zoning developed in minerals depends upon many factors, including the slope of the solidus path for the mineral. If the solidus path is steep the compositions of successive zones change only slightly even in large temperature intervals, but if the slope is gentle a wide range of zoning can be developed in a small temperature interval.

The System Diopside-Anorthite-Albite

The main features of this system are summarized in Figs. 1 and 2, and a comprehensive account of equilibrium and fractional crystallization for various liquids has been presented by Bowen (1915). It is now known that the phase relationships are more complex than indicated, because appreciable substitution of alumina occurs in the pyroxene (Hytönen and Schairer, 1961). Schairer and Yoder (1960) have shown that there is no eutectic on the join diopside-albite, but that the point labeled C in Fig. 2 is a piercing point at a considerable higher temperature, 1133° C. However, revised data for the whole system are not available, and it will be assumed in the following discussion that the system remains ternary. Since most of the compositions considered lie in the plagioclase field, departures from ternary behavior probably have little effect on the general pattern of crystallization.

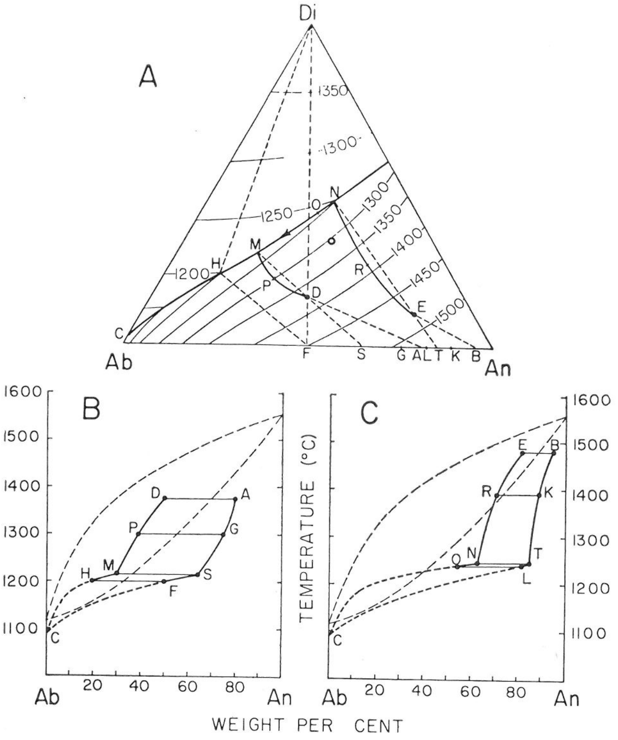

Fig. 2. Equilibrium crystallization in the system diopside-anorthite-albite.

A. Crystallization of liquids D and E, after Bowen (1915). For explanation see text and Bowen's paper. The open circle is the projected composition of Nockold's (1954) average "central" basalt (see text and Fig. 3).

B and C. Perspective TX projections of the liquidus and solidus paths for the liquid D (DPMH and AGSF) and for the liquid E (ERNO and BKTL) in Fig. 2A. With fractional crystallization, these paths would continue down the heavy dashed curves to C. The liquidus and solidus for the system anorthite-albite are shown as light dashed curves.

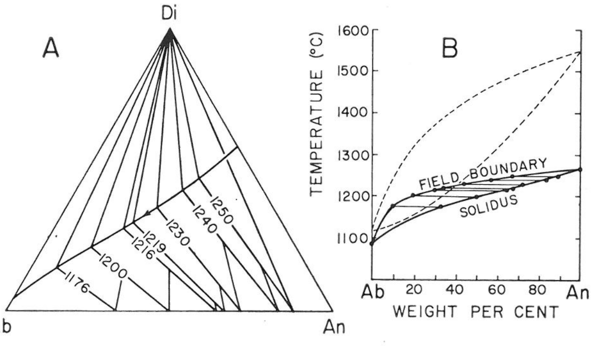

Fig. 1. The system diopside-anorthite-albite, after Bowen (1915).

A. Three-phase triangles measured by Bowen.

B. Perspective TX projection of the solidus and the liquidus field boundary. Three-phase triangles project as horizontal lines connecting pairs of points on the field boundary and solidus. The liquidus and solidus for the system anorthite-albite are shown as dashed curves (Bowen, 1913).

Each liquid on the field boundary coexists with diopside and a plagioclase feldspar of fixed composition, and the three phases coexisting at each temperature are represented by the corners of a three-phase triangle. Those experimentally measured by Bowen are illustrated in Fig. 1A. During crystallization, the liquid and the plagioclase feldspar are enriched in albite relative to anorthite. The extent of this enrichment is indicated by the ratio of albite/anorthite (Ab/An), and it is illustrated in Fig. 1B, a projection of the field boundary and of the solidus from within the TX prism on to the An-Ab-T face of the prism. The three-phase triangles project as lines connecting pairs of points on the field boundary and the solidus. The proportion of diopside in the liquid is not represented because the projection is made horizontally through the diopside-T edge. Liquidus and solidus boundaries for the system anorthite-albite (Bowen, 1913) are plotted for comparison. Ternary crystallization temperatures are lower and, except near albite, the projected ternary field boundary and the solidus both slope much more gently than in the binary system. The difference in composition between coexisting liquid and plagioclase in terms of the ratio Ab/An is smaller in the ternary system than in the binary system. This is also true for plagioclase precipitated from multicomponent magmatic liquids (Wager, 1960a, Fig. 12).

Addition of other components to the system, in moderate amounts, would cause the field boundary to generate a surface with the form of a shelf. The boundary is only a line passing across this shelf, but, for convenience, whenever this feature appears on a liquidus or solidus path it will be referred to as a shelf.

Bowen described the equilibrium crystallization of the mixtures D and E in Fig. 2. The liquid D follows the path DPMH while the plagioclase changes composition from A to F, and the liquid E follows the path ERNO while the plagioclase changes from B to L. The enrichment of liquid and plagioclase in the ratio Ab/An is illustrated by the liquidus and solidus paths in Figs. 2B and C. These diagrams were obtained in the same way as Fig. 1B, by projecting the tie-lines for coexisting liquid and plagioclase. Liquidus and solidus paths in the binary plagioclase system are plotted for comparison. When plagioclase crystallizes alone from a ternary liquid the projected liquidus and solidus paths are steeper than in the binary system, but as soon as plagioclase is joined by diopside they become less steep than in the binary system. It should be noted that the slope of a projected liquidus path is not the same as its actual slope on the liquidus surface. However, although the slopes of the paths DPM and ERN are not quite as steep as indicated in the projection, they are steeper than the slopes in the binary system during the corresponding composition intervals (compare Figs. 2A, 2B, 2C).

The slopes of the liquidus paths in these projections may be considered as measures of differentiation of the liquid. The steep slopes DM and EN indicate that little differentiation occurs while plagioclase alone crystallizes from a multicomponent liquid, whereas the gentle slopes MH and NO indicate that when plagioclase is joined by other crystalline phases much differentiation occurs in a small temperature interval.

The influence of the slopes of liquidus paths on the rate of crystallization of liquids is demonstrated by Bowen's data for the liquids D and E (Fig. 2A). Liquid D begins to crystallize at 1,375° C., and approximately 50% crystallizes while its composition changes from D to M in a temperature interval of 159° C. The remaining 50% crystallizes while it changes composition from M to H in a temperature interval of only 16° C. Similarly, approximately 75% of liquid E crystallizes along the path EN in a temperature interval of 235° C. and the remaining 25% crystallized along the path NO in a temperature interval of only 8° C.

Bowen also discussed fractional crystallization in this system. Continuous zoning of the plagioclase lowers the temperature of final consolidation, and causes enrichment of the liquid, and of the outer plagioclase zones, in the ratio Ab/An. The liquids D and E then follow paths similar to those illustrated in Figs. 2B and C, with two modifications. The liquidus paths DPM and ERN, and the solidus paths AGS and BKT become somewhat less steep, joining the projected field boundary and solidus at temperatures lower than those indicated by MS and NT. However, Bowen's diagrams confirm that the paths for these compositions remain steeper than the corresponding paths in the binary system. The final liquid persists to much lower temperatures than indicated by HF and OL, and with strong fractionation the late liquids, and the outer plagioclase zones, could continue to the point C, the albite-diopside eutectic (assuming, for convenience, that the albite-diopside join remains binary).

Fusion processes can be traced by following the liquidus and solidus paths in the direction of increasing temperature. Partial fusion of the crystalline mixtures D and E, composed of diopside and homogeneous plagioclase feldspar, produces first a trace of liquid with compositions H and O, respectively. Because these liquids lie on the shelf, small increases of temperature are followed by considerable melting as the liquid changes composition up the gentle slope of the shelf. Once the liquid leaves the shelf (at M and N respectively), much larger temperature increases are required to cause much further melting or change in liquid composition. For example, if equilibrium is maintained, an increase in temperature of 16° C. is sufficient to melt 50% of the mixture D while the liquid changes from H to M, but a further increase of 159° C. is required to melt the remaining 50%. Even if equilibrium is not maintained, *i.e.* if the crystalline plagioclase fails to react continuously with the liquid developed, the general pattern is unchanged. If the mixture D is composed of diopside and zoned plagioclase crystals, the first liquid developed is richer in the ratio Ab/An than H, and it forms at a lower temperature.

HAPLOBASALTIC, HAPLODIORITIC AND HAPLOGRANITIC MAGMAS

The compositions of many igneous rocks can be represented approximately in the system diopside-anorthite-albite-orthoclase-silica. Bowen (1915) pointed out the close chemical and mineralogical correspondence of some natural basalts and diorites with mixtures lying close to the field boundary in the system diopside-anorthite-albite. The assemblages labradorite+diopside and andesine+diopside, with bulk compositions lying close to the field boundary, he called haplobasaltic and haplodioritic, respectively. Liquids with these compositions were similarly called haplobasaltic and haplodioritic magmas. Haplogranitic compositions lie close to the system albite-orthoclase-silica, but if these compositions are projected from within the five-component system onto the system diopside-anorthite-albite, with orthoclase+albite+silica plotted jointly as albite, they are represented by points not far removed from the field boundary in the system diopside-anorthite-albite. Therefore, although the assemblage albite+diopside (with bulk composition close to the field boundary) is not closely related in composition to granites, it is considered useful in this review to refer to this assemblage as haplogranitic. The assemblage oligoclase+diopside can be referred to as haplogranodioritic. These terms are used in Fig. 3.

It is often stated that typical basalts are composed essentially of labradorite and pyroxene, and that these minerals begin to crystallize almost simultaneously (Bowen, 1928, pp. 64–69; Hess, 1960, p. 178). This has been demonstrated experimentally for some basalts by Yoder and Tilley (1957). Such basalts are described as "normal" in this paper to distinguish them from what are here referred to as "olivine-," "pyroxene-," and "feldspar-basalts." "Olivine-basalts" precipitate olivine first, followed later by plagioclase and pyroxene. "Pyroxene-" and "feldspar-basalts" first precipitate either pyroxene or plagioclase, respectively. Normal basalts correspond to haplobasaltic compositions lying on the field boundary in the system diopside-anorthite-albite. Pyroxene-basalts correspond to haplobasaltic compositions lying in the diopside field, and feldspar-basalts correspond to haplobasaltic compositions lying in the plagioclase field. Nockold's (1954) average "central" basalt is plotted in Fig. 2A in terms of its normative pyroxene and plagioclase; it corresponds to a feldspar-basalt. Liquidus and solidus paths for a haplomagma with the composition of this point in the system diopside-anorthite-albite (feldspathic haplobasaltic magma) can be estimated from Bowen's (1915) data, and the result is shown in the projection of Fig. 3.

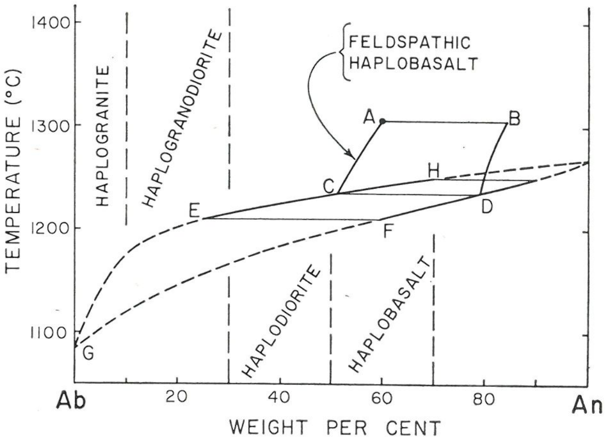

FIG. 3. Perspective TX projection of the liquidus and solidus paths (ACE and BDF) for equilibrium crystallization of the feldspathic haplobasaltic magma, A, representing the "central" basalt projected onto Fig. 2A. With fractional crystallization the paths would continue down the heavy dashed lines to G (the lettering in this figure does *not* correspond to that in Fig. 2). The liquid compositions on the path ACEG are related to their nearest igneous equivalents by their designation as haplomagmas. Normal haplobasaltic magmas lie on or close to the field boundary between C and H.

The liquid (A) begins to crystallize at 1,305° C. and, with equilibrium cooling, approximately 20% crystallizes in an interval of 70° C. (AC), while the plagioclase changes composition from about An84 to An79 (BD). Plagioclase is then joined by diopside. The remaining 80% of the liquid crystallizes in a temperature interval of only 25° C. (CE) while the plagioclase changes compositon to An_{59} (from D to F). The final liquid (E) at 1,210° C., with a ratio Ab/An of 0.75, is haplogranodioritic in composition. With strong fractional crystallization, zoning of plagioclase would cause the liquid to change composition to G, reaching haplogranitic compositions.

In order to examine the final stages of crystallization of haplogranitic magmas it is necessary to consider the effect of the additional components orthoclase and silica. Bowen (1928, pp. 104–110) briefly discussed the systems diopside-anorthite-albite-orthoclase and anorthite-albite-orthoclase-silica in connection with the crystallization of basaltic magma. Many parts of the complete five-component system have since been determined experimentally (*cf.* Schairer, 1957). The effects of adding moderate amounts of the components orthoclase and silica to mixtures corresponding to haplobasaltic magmas in Fig. 3 would be insignificant until the later stages of fractional crystallization. (During the middle and late stages of crystallization of natural magmas, the components of diopside in the synthetic system appear in hydrous phases such as amphibole and mica.) If Ab in Fig. 3 were replaced by albite+orthoclase+silica, the general pattern of fractional crystallization would be similar to that illustrated, except that the final temperature of consolidation at G would be lower, the final liquids and feldspar crystals would contain an appreciable proportion of K_2O, and quartz would be precipitated in the closing stages of crystallization. All liquidus temperatures would be somewhat lower, increasingly so for the more acid compositions. Final crystallization of haplogranitic magmas would occur near the feldspar-quartz field boundary of the Residua System, and this stage may be represented by another shelf on the liquidus surface.

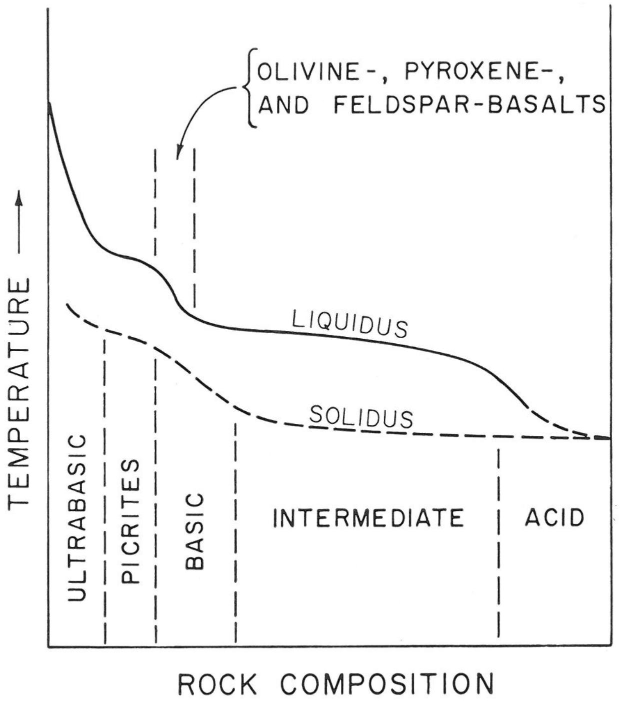

FIG. 4. Possible liquidus and solidus profiles for an igneous rock series. The liquidus profile represents one liquidus path through multicomponent space. The solidus profile does *not* represent a solidus path for any particular mineral. This tentative diagram illustrates schematically the temperatures of beginning of melting and of complete melting for a series of igneous rocks.

LIQUIDUS SLOPES FOR IGNEOUS ROCK SERIES

Combination of extrapolations from Fig. 3 with the inferences discussed above and in the earlier paper (Wyllie, 1960) provides the liquidus profile illustrated in Fig. 4. This is a tentative working model representing one possible liquidus path through the multicomponent system including all igneous rocks. The stage of differentiation can be represented by a parameter such as the differentiation index (Thornton and Tuttle, 1960). The liquidus temperatures, the gradients of the slopes, and the positions of changes in gradient probably vary from one igneous series to another. The effects of pressure, with or without volatile components, are considerable. A temperature scale on Fig. 4 would thus be meaningless unless for a specific suite of rocks under specific conditions. Thermal data of this kind are not yet available.

The liquidus profile illustrates the rate of change of liquid composition for a constant rate of temperature change during the fractional crystallization of a magma, or the fusion of a crystalline igneous rock. It should be stressed that this representation need not imply that the rocks plotted have ever existed as completely liquid magmas. Shelves extend across picritic compositions (ranging from olivine-rich basalts to peridotite), across the composition range of basic and intermediate rocks, and across acid compositions. These will be referred to as the upper, middle, and lower shelves, respectively. They are connected by steeper liquidus slopes.

Evidence for the existence of the middle shelf and the steeper slope above it is reviewed in the preceding pages. Nockolds (1936) hinted at the possible existence of a shelf feature for this compositional range when discussing the rarity of intermediate magmas in basic-acid igneous associations. He suggested that perhaps the pyroxene and plagioclase crystallized from a basic magma through a comparatively small temperature range, so that unless the residual magma was removed during a comparatively short space of time, intermediate rocks would not form.

Below the middle shelf, the liquidus slope for acid melts appears to increase in steepness (Fig. 3). The increase may be only apparent in the system diopside-anorthite-albite, because the temperature of the point G in Fig. 3 is now known to be 1133° C. (Schairer and Yoder, 1960). However, similar changes in slope occur in several systems for compositions corresponding to approximately the same stage of differentiation. In the systems leucite-forsterite-silica, leucite-diopside-silica, leucite-anorthite silica, and nepheline-anorthite-silica (illustrated in Figs. 30, 31, 32 and 35 of Schairer's useful review paper, 1957) the field boundaries separating the primary fields of forsterite, enstatite, diopside and anorthite, respectively, from the primary fields of one of the minerals of the Residua System, follow rather gently sloping paths at higher temperatures. At lower temperatures, as the field boundaries approach the Residua System, the slopes of the field boundaries increase appreciably. This increase in slope occurs with no change in the number of coexisting phases. That the steep slope at the low-temperature end of the middle shelf (Fig. 4) does exist is therefore suggested by the pattern of crystallization exhibited by several synthetic systems.

The existence of a steep liquidus slope for residual acid melts has been inferred from petrological studies. Bailey *et al.* (1924) suggested that after the crystallization of the gabbroic minerals in the Glen More ring dike, there was "a marked pause in the process of crystallization" before the granitic residuum crystallized. Holmes and Harwood (1928) suggested that after crystallization of the main part of tholeiitic sills, the residual acid liquid passed down a steeply-dipping groove in multi-dimensional space until it finally crystallized as micropegmatite.

The crystallization of the final liquid as granophyre or micropegmatite may be compared with the crystallization of liquids on the feldspar-quartz field boundary of the Residua System. From the data obtained by Tuttle and Bowen (1958, Fig. 23) it can be seen that, in a given temperature interval, much more crystallization occurs when feldspar and quartz crystallize together than when feldspar crystallizes alone. The final stages or crystallization of magmas, marked by the appearance of quartz, may thus be represented by the lower shelf indicated in Fig. 4.

A steep liquidus for the composition range including feldspar-, pyroxene-, and olivine-basalts connects the middle and upper shelves. The steep slope for feldspar-basalts is illustrated by AC in Fig. 3. A similar pattern is found for compositions corresponding to "olivine-basalts" in the system MgO-FeO-SiO_2 (Bowen and Schairer, 1935). Few basalts contain more than a small excess of either plagioclase or pyroxene, and the compositional range of such basalts may be limited to the lower part of the steep slope just above the middle shelf. There is no similar limit on the amount of olivine contained by crystalline basalts and other basic rocks (although there may be a limit on the amount of olivine contained in solution in basic magmas, as suggested by Bowen in 1928), and the liquidus path thus continues up the steep slope for rocks approaching picritic compositions. There are indications from the system CaO-FeO-MgO-SiO_2 that as the content of dissolved forsteritic olivine increases in liquids of certain compositions, at least, a steep liquidus gives way to a shelf feature. Possibly, therefore, the steep liquidus corresponding to olivine-basalts may give way to an upper shelf for picritic compositions (Wyllie, 1960). For ultrabasic rocks above the upper shelf, liquidus temperatures are high and the slope is steep.

The dashed line in Fig. 4 is a possible solidus profile reflecting the liquidus pattern of shelves and steep slopes. It is *not* a solidus path for any particular mineral.

Several liquidus profiles of this type for different igneous rock series could be represented on a surface illustrating not only the stage of differentiation but also the compositional variations between rocks at the same stage of differentiation (*e.g.* between alkaline, calc-alkaline, and tholeiitic series). The problem lies in finding suitable parameters to separate the different series (Wager, 1960b).

PETROLOGICAL APPLICATIONS

The thermal regime of a magmatic system is complex. The rate of temperature change depends upon many factors, in particular upon the heat balance between the magma, the phases crystallizing from the magma or being dissolved by it, and the regional surroundings. Most of these factors cannot be evaluated because insufficient thermodynamic data are available. For simplicity, therefore, the preliminary petrological applications which follow refer only to a constant rate of temperature change. It is unlikely that these conditions ever obtain in natural systems, but the conclusions reached by making this assumption will serve as working hypotheses. *It should be borne in mind that although only small changes of temperature are required to cause considerable melting or crystallization of compositions on shelf features, the amount of heat involved is much larger than for corresponding temperature intervals on steep liquidus slopes. The latent heat of fusion is an important item in the thermal budget.*

Applications of two types may be considered: (a) changes in the slope of liquidus paths in igneous systems may help to account for the relative proportions of various igneous rocks in different petrographical associations, and (b) the nature of continuous zoning in minerals will be dependent on changes in slope of their solidus paths.

Primary basalts. Basalts may be formed by partial fusion of feldspathic peridotite (Bowen, 1928). The intermediate magma first developed on the middle shelf (Fig. 4) increases rapidly in amount while it changes composition up the gentle slope of the shelf. Basaltic magma is formed at the high-temperature end of the shelf and on the lower part of the steep slope above it. A similar pattern would persist if the crystals involved were the high pressure phases (Yoder and Tilley, 1961). Garnet, clinopyroxene, and olivine would melt together while the liquid changed composition across the shelf, and when only liquid plus olivine remained, the middle shelf would give way to a steep slope, as illustrated in Fig. 4. Both the rate of fusion and the rate of change of composition (for a constant rate of temperature increase) decrease markedly when the steeper slope above the shelf is reached. This change in slope might well be a vital factor in limiting the products of fusion to the chemical composition of primitive basaltic magmas.

Ultrabasic magmas. If ultrabasic magmas are ever formed their composition may similarly be limited by the steep liquidus rising above the upper shelf (Fig. 4). The behavior of picritic magmas, which would lie on the upper shelf if they exist, was discussed in the previous paper (Wyllie, 1960).

Primary intermediate magmas. Partial fusion of sialic rocks in the earth's crust initially yields an acid melt. Its composition and the amount developed depend upon the bulk composition and mineralogy of the sialic rocks. When the temperature exceeds the threshold of the middle shelf (Fig. 4), rapid melting follows with the formation of large amounts of intermediate magma. If the original acid melt has not previously been separated from the rock this is incorporated in the magma. It changes composition rapidly up the gentle slope of the shelf, but its composition is limited by a steep liquidus path rising from the shelf, the exact position of which depends on the composition of the rock being fused. By the time this stage is reached, most sialic rocks would contain only a small residue of crystalline material. Other crustal rocks, more basic in composition, or containing an excess of aluminous minerals compared to compositions on the middle shelf, may retain a higher proportion of crystalline material when the liquidus path leaves the shelf. It is unlikely that the product of partial fusion of crustal rocks would reach the upper end of the middle shelf to yield a basic magma. The general pattern envisaged is illustrated in Fig. 2B, where D represents the projection of a hypothetical sialic rock from the multicomponent natural system onto the plane diopside-anorthite-albite. A process of this kind may account for the dominant role of intermediate rocks in the calc-alkaline series.

Basic-acid associations. The final liquid developed by equilibrium or moderate fractional crystallization of basalt is of intermediate composition. Strong fractional crystallization yields successively intermediate and acid liquids, and a small temperature interval suffices to change the liquid composition from basic to acid across the middle shelf. With the relatively rapid cooling which might be expected in intrusions of small or moderate size, the intermediate liquid stage is therefore unlikely to be represented by rocks of intermediate composition (*cf.* Nockolds, 1936). It is, however, represented by zones in plagioclase feldspar and in ferromagnesian minerals.

Hybridization. Acid magma developed by fractional crystallization of basic magma persists, with little crystallization and little change in composition, while the temperature falls from the middle to the lower shelf (Fig. 4). Hybridization could occur between the acid magma and the crystalline basic rocks during the interval of slow crystallization. Indeed, this drop from the middle shelf, if it exists, could be the cause of the hybridization which occurs in many basic-acid associations (*e.g.* Bailey *et al.*, 1924).

Oscillatory zoning. It has proved difficult to explain

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[1] In other circumstances, if conditions are such that the heat of crystallization is lost only by conduction then the rate of crystallization on the shelf feature may be retarded, leading to the development of a wide range of intermediate differentiates.

the oscillatory zoning exhibited by plagioclase feldspars in terms of the steep solidus path for the system anorthite-albite (*e.g.* Hills, 1936). However, the various explanations which have been proposed appear much more feasible if the plagioclase solidus path is gentle in the appropriate composition range. Figures 1B and 3 suggest that this could be the situation for many magmas ranging in composition from basic to intermediate.

Marginal zoning. A feldspathic basaltic magma may precipitate plagioclase before other crystalline phases. The solidus path for the plagioclase is then characterized by a steep slope followed by a shelf, as illustrated in Fig. 3. This leads to the precipitation of plagioclase crystals of fairly uniform calcic composition (solidus path BD), or crystals of fairly uniform calcic composition with narrow, marginal zones (BD followed by DF). Both types are present in rocks of the porphyritic central magma type in Mull (Bailey *et al.*, 1924, p. 241 and p. 369), and in the Stillwater complex (Hess, 1960, p. 41). Olivine crystals precipitated from basic magmas may follow similar solidus paths.

Crystals in two generations. Many petrologists have stressed the fact that a mineral may give the appearance of crystallization in two generations, although crystallization was perfectly continuous (*e.g.* Hawkes, 1930). The liquidus and solidus paths illustrated in Fig. 3 illustrate one of the ways in which this appearance could result during continuous crystallization of a feldspathic basalt. Crystallization of the magma on the slope AC produces a few large crystals of plagioclase with fairly uniform composition. When the plagioclase is joined by diopside (which can be regarded as representing the other minerals precipitated from the magma) crystallization on the shelf CE causes precipitation of many smaller plagioclase crystals, in addition to the marginal zones formed around the existing large crystals. Calcic plagioclase phenocrysts in basic rocks therefore need not represent intratelluric crystallization. A similar conclusion may be valid for olivine phenocrysts in some basic rocks.

CONCLUDING REMARKS

Phase relationships in several synthetic systems indicate a pattern for liquidus and solidus paths which is characterized by changes in the slopes of these paths. Possibly, therefore, a similar pattern applies also in natural systems. A rather abrupt change in slope occurs on a liquidus path whenever a new crystalline phase appears in the system. This occurs at the high-temperature end of the middle shelf where olivine (or more rarely, plagioclase or pyroxene) is joined by other phases, and at the high-temperature end of the lower shelf where quartz begins to crystallize. The changes in slope illustrated at the low-temperature ends of the middle and upper shelves in Fig. 4 may not persist in the natural systems (although changes of this kind, involving no change in the number of phases, do exist in several synthetic systems) because they could be smoothed out either by fractional processes or simply by the presence of additional components. The writer intends to study the melting relationships of series of rocks in the appropriate compositional ranges in order to test the hypothesis embodied in Fig. 4 (*cf.* Wyllie, 1960). If these studies confirm the suggested liquidus profile, this introduces a "tempo" into igneous processes which may help to explain some petrogenetic problems.

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DISCUSSION

E. H. ROSEBOOM, JR. (Washington, D. C.): There are theoretical difficulties to predicting zoning by means of phase diagrams. There are only two types of crystallization which we can discuss on a theoretical basis, perfect equilibrium crystallization and perfect fractional crystallization. Dr. Wyllie has used the former in his diagrams to illustrate zoning. However, by definition the crystals react perfectly to maintain equilibrium and thus no zoning can occur. In perfect fractional crystallization, the bulk composition by definition equals the liquid composition and the lever law cannot be used to predict how the proportions of the crystals and liquid will change with temperature.

P. J. WYLLIE: I agree completely with Dr. Roseboom's statements, and I hope that the complete text will answer the query. The diagrams do illustrate only perfect equilibrium conditions, and they are used in most of the text to describe equilibrium conditions. It is then pointed out that with perfect fractional crystallization (for the original compositions used in this paper) liquidus and solidus paths follow patterns similar to those illustrated for perfect equilibrium crystallization; the changes in slope are less abrupt. Conditions in natural environments probably lie somewhere between perfect equilibrium and perfect fractional crystallization, and liquidus and solidus paths in natural systems may therefore be characterized by slopes similar to those illustrated. The equilibrium diagrams can not give the range of zoning developed with fractional crystallization, but in view of the foregoing remarks, they do give an indication of the differences between the ranges of zoning which could be developed when (a) paths are steep, and (b) paths cross gentle slopes. In the brief sections dealing with tentative applications to zoning in minerals, the equilibrium diagrams have been used in this qualitative fashion.

H. D. MEGAW (Cambridge, England): Does Dr. Wyllie think that there can be any explanation of the shape of these curves in terms of what we know of felspar structure? Anorthite has perfect Si/Al alternation; this seems to be a very stable pattern. As we move away from the pure anorthite composition, the perfect order *can* still be maintained within domains—and recent structural work suggests that it *is* maintained—the substitutions being segregated in domain boundaries, perhaps one or two cells thick. When compositions are too far from anorthite, this can not be maintained without great complication. Good order is not found again till low albite, if then. Is this apparent preference for the Si/Al pattern of anorthite not likely to have a bearing on the course of crystallization?

P. J. WYLLIE: I am tempted to answer "yes" to such an elegant proposal. However, a similar change occurs in most systems when a crystalline phase exhibiting solid solution is joined by another crystalline phase. An example is provided by the system MgO-FeO-SiO_2, when olivine is joined by pyroxene, and here there is no ordering of Si and Al to consider. Among the controlling factors are the composition and amount of material being subtracted from the liquid phase. When a new phase begins to crystallize, both these factors change discontinuously, and together they cause discontinuities in liquidus and solidus paths.