

AMPHIBOLE FRACTIONATION IN CALC-ALKALINE MAGMA GENESIS

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ABSTRACT. Many experimental and petrological models for the origin of andesite have considered this rock type in isolation from other members of orogenic volcanic suites. Basalts, having chemical and petrographic affinities with andesites, occur in most calc-alkaline provinces. Hence, models that envisage andesite as a fractionation product of basalt should be considered as well as those that imply that andesite is a primary magma. Studies of simple systems and natural materials over the range 2 to 10 kb water pressure indicate that amphibole is an important near-liquidus phase in basic and intermediate magma compositions. Major element and petrological characteristics of andesites may be explained satisfactorily by crystallization of hornblende from hydrous basaltic magmas.

INTRODUCTION

Recently there have been some excellent reviews of currently advocated hypotheses for the origins of andesites (Wyllie, 1973; Boettcher, 1973; Ringwood, 1974). All these authors refer to amphibole fractionation from basalt as a method of producing the chemical characteristics of andesite. However, a critical discussion of this model has not been presented because of the scarcity of experimental data. Subsequently, several experimental studies have examined amphibole stability and its effect on magma composition over a considerable range of conditions (Holloway and Burnham, 1972; Cawthorn, Curran, and Arculus, 1973; Eggler and Burnham, 1973; Helz, 1973; Mysen, 1973; Boettcher, Mysen, and Modreski, in press; Cawthorn, in press). With these new data it is possible to re-examine the hypothesis of amphibole crystallization and andesite genesis in greater detail.

MODELS OF ANDESITE MAGMA GENERATION

One of the first experimental studies on andesites was performed by Osborn (1959) who suggested that the lack of iron enrichment in calc-alkaline suites could be attributed to magnetite fractionation. Data on atmospheric-pressure melting of natural calc-alkaline rocks by Brown and Schairer (1971) showed that liquidus temperatures do not decrease with apparent geochemical evolution in the suite. Eggler and Burnham (1973) studied the phase relationships of natural andesite up to 10 kb water pressure using the quartz-magnetite-fayalite buffer and concluded that magnetite may not be stable at high temperature above 2 kb water pressure. Biggar (1974) showed that some typical basaltic compositions would only begin to crystallize magnetite as a near-liquidus phase at oxygen fugacities greater than 10^{-6} b at 1 atm. This is in very good agreement with the data of Osborn (1969) who suggested an oxygen fugacity of 10^{-6} b for magnetite fractionation at 1 kb water pressure. These oxygen

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fugacities are unrealistically high when compared to the estimated values for andesites determined by Fudali (1965).

Kuno (1968) calculated the proportion of gabbro or magnetite gabbro that would be required to fractionate to produce a change in liquid composition from a high-alumina basalt to basaltic andesite, or to andesite, or to andesitic dacite. His estimates ranged from 70 to 98 percent (Kuno, 1968; p. 154-155). This implies that for each unit volume of erupted magma of basaltic andesite to andesitic dacite there should be between 2 and 49 units of low-pressure cumulus material. The scarcity of such rock-types either as nodules or in eroded terrane argues against such a process as a general model.

The composition of magmas derived from the mantle by partial melting may be critically dependent upon water content. For example, partial melting of aluminous peridotite with water pressure equal to total pressure in the range 10 to 25 kb may produce a basaltic andesite or andesitic liquid (O'Hara, 1965; Yoder, 1969; Kushiro, 1972; Kushiro and Yoder, 1972; Green, 1973). At lower partial pressures of water the liquid may be either nephelinitic or tholeiitic depending upon the degree of melting (Green, 1969, 1973). Under dry conditions at the same pressures, partial melts may be olivine tholeiites or slightly nepheline-normative (Kushiro, 1968; O'Hara, 1968). Mysen (1973) presented data suggesting that the change in magma type from silica-oversaturated to silica-undersaturated produced from a sample of a spinel peridotite nodule may occur if P_{H_2O} decreased to $< 0.5 P_{total}$ at high pressure. Thus, while andesite-like compositions may be derived from the mantle as a primary magma, it remains to be demonstrated that there is sufficient water in the upper mantle for this to happen.

Partial melting of subducted oceanic crust may also produce andesitic liquids. At shallow depths (15-40 km), partial melting of amphibolite could produce such liquids (Holloway and Burnham, 1972). Partial melting of dry quartz eclogite in the depth range 80 to 150 km may also give rise to andesite (Green and Ringwood, 1968), although this latter hypothesis has been questioned by Stern (1974) who suggested that partial melts of eclogites would require extensive modification (fractionation?) before they approached calc-alkaline compositions. Fractionation of garnet or garnet pyroxenite (Green and Ringwood, 1968) must be questioned, because Gill (1974) showed that the REE pattern of andesites was not consistent with the removal of garnet.

The geometrical relationship between subducted oceanic plate and magma generation implies that volcanic activity overlies regions where the depth to the Benioff zone is 70 to 220 km (Dickinson, 1968). Amphibolite will dehydrate to eclogite and vapor at depths of less than 70 km (Nishikawa, Kushiro, and Uyeda, 1971; Lambert and Wyllie, 1968), unless it is stabilized to higher pressures by components such as fluorine, about which little is known as yet. Hence, if amphibolite melts, it must do so at too shallow a depth to explain the geometrical relationships between orogenic volcanism, location of trench, and depth of earthquakes. Further-

more, the liberation of water by this process is at too shallow a depth to support the argument that dehydration of oceanic plate and hydration of overlying mantle may explain the generation of andesite from the mantle (McBirney, 1969; Green, 1973; Nicholls and Ringwood, 1972; Ringwood, 1974). An alternative source of H₂O for this process is dehydration of serpentine in the uppermost oceanic mantle. However, it is unknown yet whether there are sufficient quantities of serpentine and whether it is stable at the temperatures generated in the 70 to 200 km depth region of the subduction zone.

The formation of andesite by partial melting of eclogite at below 80 km (Green and Ringwood, 1968) demands that this magma be erupted from these depths without undergoing any crystallization or modification. Osborn (1962) has questioned whether this liquid could be in contact with an olivine-rich wall rock during ascent without reacting with it. The temperature at which Green and Ringwood (1968) generated the andesite is 1380°C at 30 kb. This is higher than the solidus of anhydrous lherzolite at pressures less than 20 kb and much higher than the water-saturated solidus (Kushiro, Syono, and Akimoto, 1968). Hence, considerable reaction is expected.

Basaltic magma is frequently associated with andesite and may even be volumetrically greater than andesite (for example, Baker, 1968; Miyashiro, 1974). High degrees of melting of oceanic tholeiite are required to produce andesite. Hence, there would be very little residual material left to produce basaltic magma even if high enough temperatures to melt this residual material could be generated. The volume of basalt produced would probably be small relative to andesite.

Models that envisage andesite as a primary partial melt of aluminous peridotite in the upper mantle under hydrous conditions (Kushiro, 1972) demand that the magma be erupted from depth without undergoing any crystallization. This becomes a serious problem with hydrous liquids that have a negative dT/dP slope for the liquidus at crustal pressures. Hence, some crystallization of hydrous andesitic magma would be expected before eruption. The great abundance and variety of phenocrysts in calc-alkaline rocks likewise suggests that substantial crystallization at lower pressure has occurred (O'Hara, 1968).

Some supporting evidence that andesites are not equilibrium partial melts from currently postulated upper mantle compositions may be found in the Fe/Mg ratios of andesitic magmas. Roedder and Emslie (1970) showed that the partition coefficient¹, K_D, for Fe²⁺ and Mg between olivine and liquid was approximately 0.3 at 1 atm. Hence, a liquid in equilibrium with mantle material containing Fo₉₃ should have a value of 0.80 for Mg/(Fe²⁺ + Mg). Andesites have a very much lower value than this (see discussion in Mysen and others, 1974). Mysen (1974) has attempted to reinvestigate this problem using total iron contents rather

$$^1 K_D = \left(\frac{\text{Fe}}{\text{Fe} + \text{Mg}} \right)_{\text{ol}} / \left(\frac{\text{Mg}}{\text{Fe} + \text{Mg}} \right)_{\text{ol}} \times \left(\frac{\text{Mg}}{\text{Fe} + \text{Mg}} \right)_{\text{L}} / \left(\frac{\text{Fe}}{\text{Fe} + \text{Mg}} \right)_{\text{L}}$$

than Fe^{2+} . He concluded that under sufficiently oxidizing conditions, olivine Fo_{94} could be in equilibrium with a relatively iron-rich liquid at 15 kb. Under reducing conditions (using the iron-wustite buffer), he suggested a liquid with $\text{Mg}/(\text{Mg} + \text{Fe})$ equal to 0.84 was in equilibrium with an olivine Fo_{92} . This suggests a value for the partition coefficient of 0.46. Under these conditions there should be very little Fe^{3+} in the liquid (Roedder and Emslie, 1970, p. 280). Hence, this K_D value should approximate to the average K_D determined by Roedder and Emslie (1970). As there is a significant difference, either K_D values are extremely pressure-sensitive or the electron microprobe analyses of the hydrous glasses are incorrect (Cawthorn and others, 1973). We suggest that metastable quenching products which altered the quenched liquid composition have formed. Hence Mysen's (1974) data may not be quantitatively valid. We have no evidence for exceptionally high oxygen fugacities in andesitic magmas (Fudali, 1965) which is a prerequisite for producing andesite as a direct partial melt from hydrous mantle (Mysen and Kushiro; "Comments to the reply", in Mysen and others, 1974). Hence, we concur with Nicholls and Ringwood's observations on $\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$ values in this published discussion.

Fractional melting of a hydrous upper mantle could explain the range of compositions from basaltic through andesitic observed in calc-alkaline suites. Liquids produced by such a mechanism may show a discontinuous chemical variation, although compositional variation could be smeared out by very minor subsequent fractionation (Presnall, 1969). Kuno's (1968) observations on the volcanic suites of Japan suggest that the calc-alkaline suite (Kuno's hypersthenic series) lies between tholeiitic and alkalic provinces. These latter two suites are assumed to show fractionation crystallization trends. We, therefore, find it difficult to accept that the geographically intermediate suite (the boundaries of which are entirely gradational) are produced by the process of fractional melting.

The stability of amphibole near to the liquidus for several basic compositions has been examined by Yoder and Tilley (1962) and Holloway and Burnham (1972) over a pressure range 2 to 10 kb and with water pressure both less than and equal to total pressure. Hence, consideration of the geochemical effects of crystallization of amphibole is relevant to studies on calc-alkaline magma genesis. Cawthorn (in press) has determined the stability of pargasitic hornblende at 5 kb pressure in a wide range of simple basalt-like compositions and predicted evolution paths for water-saturated basic magma compositions. The following sections consider the geochemical and petrological implications of these studies.

PHASE DIAGRAMS IN THE SYSTEM $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-Na}_2\text{O-H}_2\text{O}$

In the simple system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-Na}_2\text{O}$ at 5 kb pressure under water-saturated conditions, the thermal stability of hornblende and the range of compositions from which it will crystallize are largely dependent upon the Na_2O content of the liquid (Cawthorn, in press). Amphibole will not crystallize from a liquid containing less than 3

percent Na_2O . (This does not mean that a *bulk composition* with less than 3 percent Na_2O will not crystallize amphibole above the solidus. Such a bulk composition may crystallize Na_2O -free phases near the liquidus, causing an increase in the Na_2O content of the residual liquid to more than 3 percent, whereupon amphibole may crystallize.) Above this threshold value, the likelihood of major amphibole crystallization increases, this mineral replacing plagioclase and/or spinel as the aluminous phase. If the course of crystallization of a bulk composition which always produces liquids with less than 3 percent Na_2O is being considered, the phase relations of Yoder and Chinner (1960), Yoder (1965, 1966), Yoder and Dickey (1971), and Ford and O'Hara (1972) in the system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ may yield good approximations to the behavior of such natural hydrous magmas. However, if the liquid composition at any stage contains more than 3 percent Na_2O , amphibole crystallization may be encountered, and the phase diagrams presented here apply.

Diagrammatic representation of compositional phase diagrams (as opposed to P-T phase diagrams) becomes more difficult as more components are introduced. Three-dimensional phase diagrams have been presented (for example, Osborn, 1959; Kushiro, 1970), but to a non-specialist in experimental petrology they are often difficult to visualize. O'Hara (1968) attempted to eliminate these perspective problems by presenting projection diagrams within a quaternary system². The resultant triangular diagrams may be interpreted in exactly the same way as any other pseudoternary system, provided the projection phase is encountered in all the equilibria considered. In this way a four-component system may be investigated and interpreted by a series of pseudoternary diagrams. The addition of H_2O adds no complications to this technique provided the equilibria are all water-saturated. The data are regarded as projections from vapor, assumed to be pure H_2O .

Pargasite is the simplest amphibole end-member which can be taken to approximate to natural igneous hornblendes. It requires the addition of another component — Na_2O — to the system used by O'Hara (1968) and adds another dimension to the diagrams. Hence, the pseudoternary diagrams projected from a mineral composition and from water become pseudoquaternary. Two of the most useful projection diagrams in O'Hara's (1968) scheme are projections from olivine into the plane $\text{CaSiO}_3\text{-MgSiO}_3\text{-Al}_2\text{O}_3$ and from diopside into the plane $\text{CaAl}_2\text{O}_4\text{-MgO-SiO}_2$. The phase diagrams produced in the pseudoquaternary systems that contain these base planes and have Na_2O as the apices of the tetrahedra are shown in figure 1. It is not possible to represent a point unambiguously in this kind of perspective diagram. Hence, we have cut a series of sections parallel to the base planes, such that each section contains a fixed Na_2O content. The phase relations in these sections and a more detailed discussion of their geometry and construction are presented elsewhere

² A computer program for calculating parameters in these projection diagrams is available from R. G. Cawthorn.

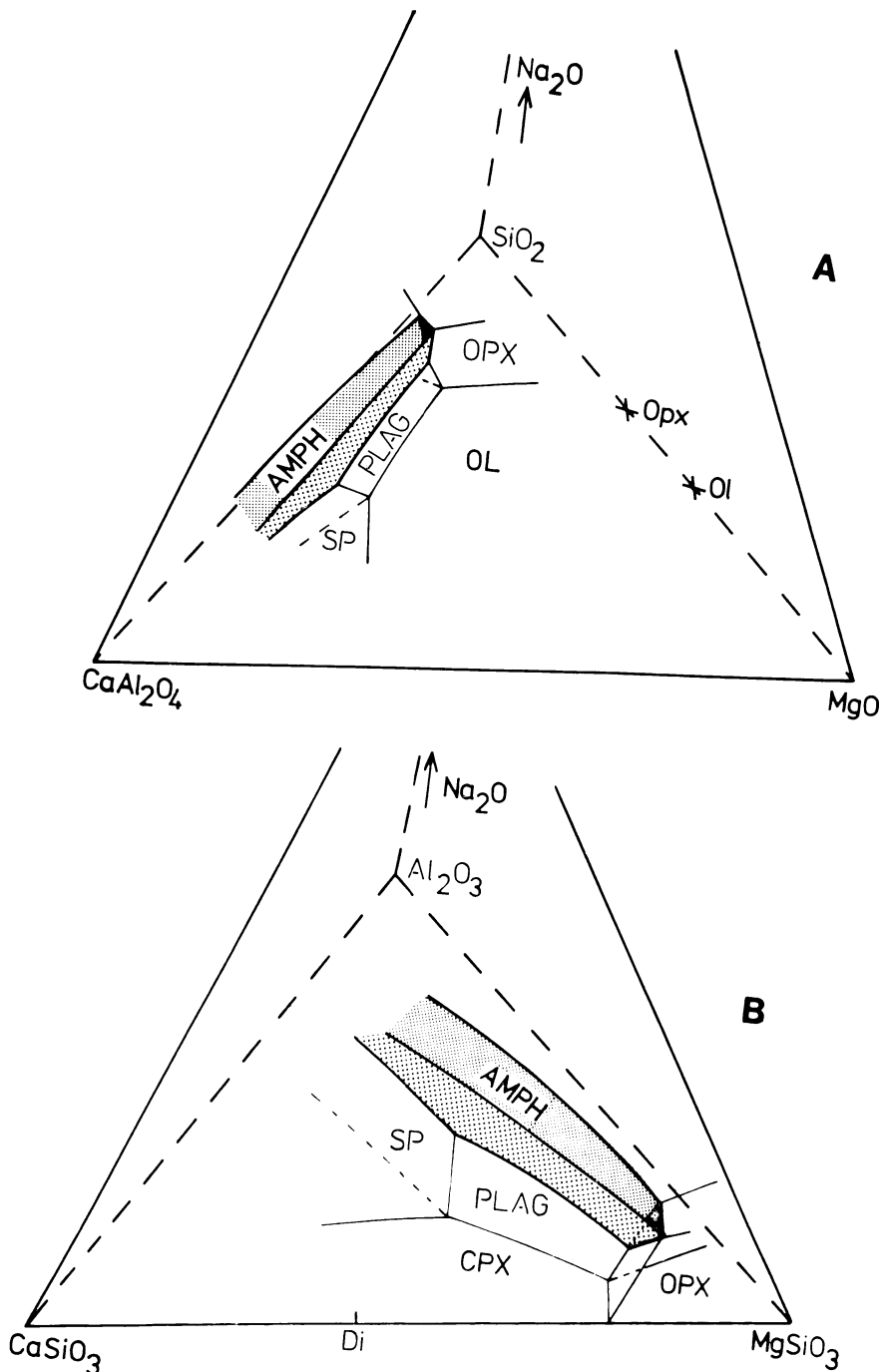


Fig. 1. A. Phase relations within the volume CaAl_2O_4 - MgO - SiO_2 - Na_2O projected from diopside under 5 kb with excess vapor. SiO_2 lies at the back of the tetrahedron in this view. The amphibole volume (shaded for emphasis) does not intersect the base plane (CaAl_2O_4 - MgO - SiO_2). The lowest Na_2O level at which it occurs is 3 percent. The range of amphibole stability widens with increasing Na_2O content.

B. Phase relations within the volume CaSiO_3 - MgSiO_3 - Al_2O_3 - Na_2O projected from olivine under 5 kb with excess vapor. Al_2O_3 lies at the back of the tetrahedron. Abbreviations: OL—olivine; Opx—orthopyroxene; Cpx—calcium-rich pyroxene; Plag—plagioclase; Sp—spinel; Amph—amphibole.

(Cawthorn, in press). We have superposed two sections, one containing 4 percent Na_2O , the other 6 percent, from each tetrahedra and presented them in figures 2 and 3. These diagrams may be treated as pseudoternary systems.

In figure 3 rock compositions are projected from an ideal clinopyroxene composition ($\text{Ca}(\text{Mg,Fe})\text{Si}_2\text{O}_6$). To be more precise the compositions should be projected from real clinopyroxene compositions (containing Al, Ti, Na, et cetera). As a consequence of the low temperatures involved in hydrous crystallization processes (about 1000°C) solid solution of clinopyroxene toward orthopyroxene will be limited. Clinopyroxenes crystallizing from silica-rich liquids show relatively little solid solution toward Al_2O_3 (Cawthorn, in press). Also as compositions of rocks presented here lie close to the plane $\text{CaAl}_2\text{O}_4\text{--MgO--SiO}_2$, the errors in projection are small. Solid solution, other than Mg-Fe, in olivine is extremely limited so that these problems do not arise in the construction of figure 2.

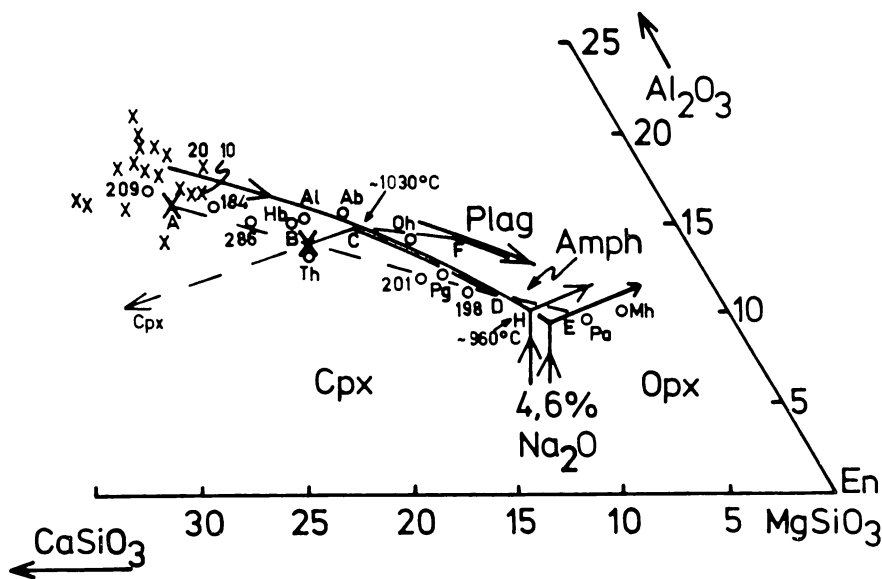


Fig. 2. Weight percent projection from olivine, vapor, and Na_2O into part of the plane $\text{CaSiO}_3\text{--MgSiO}_3\text{--Al}_2\text{O}_3$ (fig. 1B viewed from the Na_2O apex). Four and six percent Na_2O refer to the phase relations for liquids containing 4 and 6 percent Na_2O respectively. 5 kb hydrous experimental samples, after Yoder and Tilley (1962), Hb—high-alumina basalt; Th—tholciite; Al—alkali basalt; Oh—oxidized hawaiiite. After Helz (1973), PG—Picture George basalt; Ab—alkali basalt. After Cawthorn, Curran, and Arculus (1973), 209 and 184—basanitoids; 286—alkali basalt; 201 and 198—basaltic-andesites. After Eggler (1972a), Pa—Paracutin andesite. After Eggler and Burnham (1973), Mh—Mount Hood andesite. Crosses are amphiboles synthesized by Holloway and Burnham (1972); Eggler (1972b); Helz (1973); Cawthorn, Curran, and Arculus (1973). Amphiboles denoted “10” and “20” were produced at 10 and 20 kb respectively by Green (1973; tables 6 and 12). Liquid evolution trends B-C-D-E-F and points A and H are discussed in the text. Abbreviations as for figure 1.

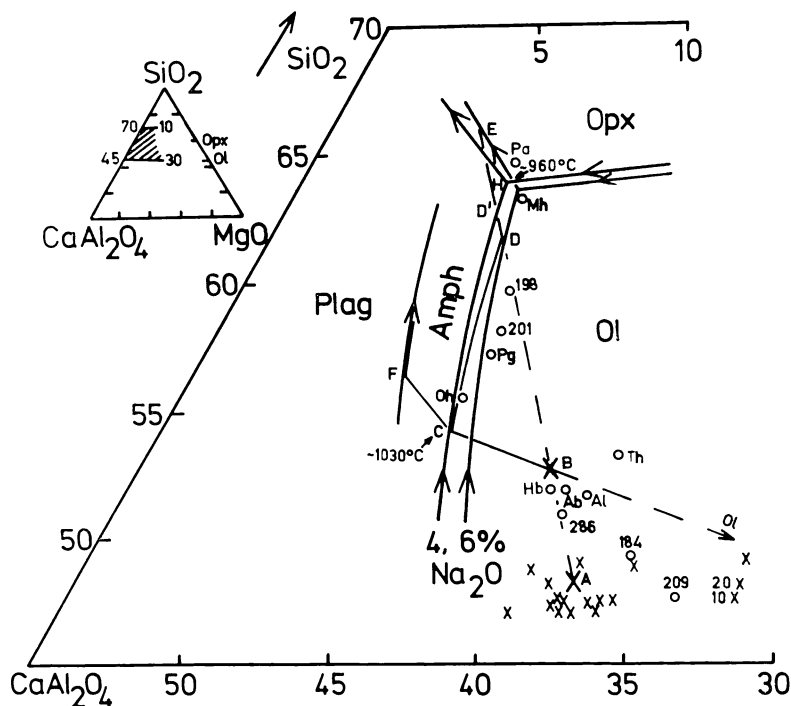


Fig. 3. Weight percent projection from diopside, vapor, and Na_2O into part of the plane CaAl_2O_4 - MgO - SiO_2 (fig. 1A viewed from the Na_2O apex), shaded inset shows region presented in the main diagram. Explanation as for figure 2.

To incorporate the results of experimental studies on natural materials a recalculation scheme based on that of O'Hara (1968) is used. The analyses of these natural examples are calculated into components analogous to the five oxides (SiO_2 , Al_2O_3 , CaO , MgO , and Na_2O) used in the simple system by the following equations (in wt percent):

$$\text{SiO}_2 = \text{SiO}_2$$

$$\text{Al}_2\text{O}_3 = (\text{molar proportions Al}_2\text{O}_3 + \text{Cr}_2\text{O}_3 + \text{Fe}_2\text{O}_3 + \text{TiO}_2) \times 101.963$$

$$\text{CaO} = (\text{molar proportions CaO} - 3.33\text{P}_2\text{O}_5 - \text{CO}_2) \times 56.08$$

$$\text{MgO} = (\text{molar proportions MgO} + \text{FeO} + \text{MnO} + \text{NiO} - \text{TiO}_2) \times 40.32$$

$$\text{Na}_2\text{O} = (\text{molar proportions Na}_2\text{O} + \text{K}_2\text{O}) \times 61.982$$

The major phases of interest in these diagrams are amphibole, orthopyroxene, and either clinopyroxene (in fig. 2) or olivine (in fig. 3). The boundaries between the liquidus fields of these phases have been located accurately in this simple system under 5 kb water pressure. The liquidus field of plagioclase has been less precisely defined in the study of the simple system. A spinel field lies toward the more Al_2O_3 -rich region in figure 2 but has not been included, as it is not involved in the following discussion. The loci of the phase boundaries in these diagrams are not sensitive to changing Na_2O content from 4 to 6 percent Na_2O . The amphibole-clinopyroxene-olivine-liquid curve for 6 percent Na_2O has

not been drawn in full on figure 2, as it coincides with the position of the curve for 4 percent Na_2O . However, two liquids projecting at the same point in these diagrams but containing 4 and 6 percent Na_2O respectively will have quite different normative mineral compositions.

To discuss the main features of the diagrams, consider a bulk composition (B) that contains 3 percent Na_2O in figures 2 and 3. The projection point of (B) is similar to that of tholeiitic basalt (examples of which are projected into figs. 4 and 5). It projects within the primary phase fields of olivine and clinopyroxene, and hence one of these will be the liquidus mineral and the other will precipitate next. By crystallization of these two phases, the residual liquid will migrate along the curve BC, increasing in Na_2O content. At point C, if about 25 percent crystallization has occurred the liquid may contain approximately 4 percent Na_2O , and the phase diagram constructed at this level may be used. (It is possible to calculate exactly the percent crystallinity of the bulk composition when the liquid composition reaches C, by using the lever rule, and hence to determine the Na_2O content of that liquid. However, approximate concentrations are sufficiently accurate for this discussion.)

Two liquid evolution paths are now possible, dependent upon whether fractional or equilibrium crystallization is considered, because there are reaction relationships involved. To test for a reaction relationship between a pair of coexisting phases and liquid, draw a tangent to the two phases-plus-liquid curve toward the tie-line joining the coexisting phase compositions. If the tangent intersects the tie-line between the phase compositions, the phases coprecipitate. If the tangent intersects an extension of the tie-line, the phase farther away from this intersection is in reaction relationship with the liquid. In figure 3 a tangent to the amphibole-olivine-liquid curve would not cut the amphibole-olivine tie-line between the two phases, but on an extension of the tie-line away from olivine. Hence, olivine reacts with liquid to produce amphibole. Likewise in figure 2 a tangent to the amphibole-clinopyroxene-liquid curve would not intersect the amphibole-clinopyroxene tie-line for most amphibole compositions. Hence, clinopyroxene is probably in reaction relationship with liquid to produce amphibole, although coprecipitation is possible.

Under equilibrium crystallization conditions the liquid will migrate along the olivine-clinopyroxene-amphibole-liquid-vapor curve CD precipitating amphibole (A). Olivine and clinopyroxene will be in reaction relationship with the liquid. The composition of amphibole crystallizing in these diagrams may be sensitive to the liquid composition and the nature of the accompanying crystallizing phases (Cawthorn, in press). However, for simplicity an average amphibole composition (A) may be used in this discussion. At point D (the intersection of the line from the amphibole composition (A) through the bulk composition (B) with the olivine-clinopyroxene-amphibole-liquid curve), the olivine and clinopyroxene will have been consumed, and amphibole only will continue crystallizing. (Olivine and clinopyroxene need not necessarily disappear

simultaneously. Hence, point D may represent two slightly different compositions in the two diagrams.) The Na_2O content of the liquid will be changing along CD, and at D it may contain up to 6 percent Na_2O . The precise Na_2O content is difficult to estimate unless the Na_2O content of the bulk composition and of the crystallizing amphibole are accurately known. If the liquid did not increase significantly in Na_2O content because of higher Na_2O contents in the amphibole, the liquid composition when all olivine was consumed might be D', which is not very different from D in figure 3. In figure 2, the olivine-clinopyroxene-amphibole-liquid locus for 4 and 6 percent Na_2O almost coincide, so D and D' would be the same point.

With subsequent crystallization the liquid will precipitate amphibole alone and hence migrate through the amphibole stability volume along curve DE (directly away from the amphibole composition). The liquid may eventually reach the orthopyroxene stability field, and amphibole and orthopyroxene will coprecipitate. In figures 2 and 3 the clinopyroxene-amphibole-orthopyroxene-liquid and olivine-amphibole-orthopyroxene-liquid curves are presented. These will not be the same as the amphibole-orthopyroxene-liquid curve. Hence, we are not justified in using these diagrams to trace liquid evolution once orthopyroxene begins to crystallize. Point E, the limit for the legitimate use of these diagrams, corresponds to the typical andesite compositions. Hence, we can predict crystallization trends from basaltic compositions through andesitic but not beyond.

Under fractional crystallization conditions, liquids of composition C will crystallize amphibole only and migrate through the amphibole volume away from the amphibole composition along CF. Once the liquid begins to crystallize plagioclase as well as amphibole, these diagrams become strictly invalid. This is because the diagrams show the cotectic curves for amphibole-plagioclase-projection phase-liquid rather than the amphibole-plagioclase-liquid cotectic curve. Hence, the plagioclase field has not been shown in full. However, it may be seen schematically that coprecipitation of amphibole and plagioclase may produce a liquid trend toward andesitic compositions.

The liquid evolution paths, represented here by DE and CF are not necessarily straight. The amphibole composition will probably change as the liquid composition changes, and hence curved paths for DE and CF are more likely. It is not possible to predict changes in amphibole composition from available data, and hence simplified linear paths have been shown.

COMPARISON OF EXPERIMENTAL DATA ON THE SIMPLE SYSTEM WITH NATURAL MATERIALS

In figures 2 and 3 data for all the natural materials that have been run under 5 kb pressure of water have been included. The data are taken from Yoder and Tilley (1962), Holloway and Burnham (1972), Eggler (1972a), Helz (1973), Cawthorn, Curran, and Arculus (1973), and Eggler

and Burnham (1973). The crystallization history of all these compositions is in agreement with the phase relationships predicted using the simple system model (except for the appearance of magnetite, spinel, sphene, apatite, and ilmenite which have been identified in the natural materials in minor proportions and excepting some of the compositions studied by Helz (1973) using a hematite/magnetite buffer). All the amphibole compositions that have been analyzed in the products of these studies have also been incorporated in the diagrams and are similar in these projections to the amphibole compositions obtained by Cawthorn (in press) in the simple system.

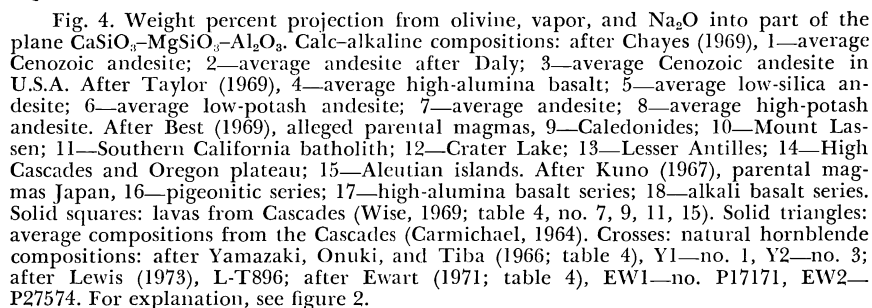
In the system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-Na}_2\text{O-H}_2\text{O}$ analogues of all the major phases reported in studies on natural materials may be produced, and crystallization histories for the simple system and natural materials appear to be similar. It is, therefore, suggested that the phase diagrams outlined by the simple system describe the behavior of natural materials sufficiently closely to justify their use in discussing the evolution of hydrous basic and intermediate magmas. The combination of $\text{Na}_2\text{O} + \text{K}_2\text{O}$ in natural samples does not appear to produce any major changes in the relationships providing $\text{Na}_2\text{O} > \text{K}_2\text{O}$. Subsequent discussions will assume that the total alkali content of natural materials would have an effect on phase relations comparable to that of Na_2O alone for the simple system.

CRYSTALLIZATION OF BASALTIC AND ANDESITIC MAGMAS

Peacock (1931) showed that magmas of calc-alkaline suites contain at least 2 percent alkali (as oxides) and generally in excess of 3 percent, even for the basaltic members. Average andesite analyses (Chayes, 1969; Taylor, 1969) contain from 4.1 to 6.3 percent equivalent Na_2O (see calculation on p. 316). Hence, the phase relationships presented in figures 2 and 3, for liquids containing 4 and 6 percent alkalis may be suitable for interpreting the evolution of the calc-alkaline suite.

We have plotted in figures 4 and 5 the average andesite compositions discussed by Chayes (1969) and Taylor (1969), the various calc-alkaline parental magmas and average compositions of andesitic provinces from Best (1969), and the parental magmas of the three volcanic provinces of Japan from Kuno (1967). As examples of the composition of amphiboles in cumulus blocks in calc-alkaline volcanics, two analyses of hornblende from gabbroic inclusions from Nigata Prefecture (Yamazaki, Onuki, and Tiba, 1966), one hornblende from a nodule from St. Vincent (Lewis, 1973), and two phenocrysts from lavas (Ewart, 1971) are included in the diagrams.

The possible crystallization sequence of a hydrous basic or intermediate magma may be considered in the same way as in the simple system. The range of most basaltic compositions in figures 4 and 5 is fairly close to point B, and their crystallization history may follow similar trends to that of composition B discussed above. The exact location of point D where clinopyroxene (in fig. 2) and olivine (in fig. 3) disappear will de-



pend upon the intersection of the line from the crystallizing amphibole through the bulk composition with the amphibole-olivine (or clinopyroxene)-liquid curve. Thus unless the exact amphibole composition crystallizing from a given bulk composition is known the precise location of D cannot be determined. The position of most of the amphibole analyses suggests that olivine, clinopyroxene, and amphibole may coexist in a basic composition over quite a large temperature interval (as D would occur close to the peritectic point involving orthopyroxene) under equilibrium crystallization conditions. Under fractional crystallization conditions, once a point comparable to C in figures 2 and 3 has been reached, the liquid would migrate directly away from the amphibole composition following a path close to the clinopyroxene-amphibole-liquid curve in figure 4. The location of the natural amphibole, Y1, in figure 4 and a few of the experimentally produced amphiboles in figure 2 lie within the amphibole primary phase field and imply that clinopyroxene may not be in reaction relationship with liquid to produce am-

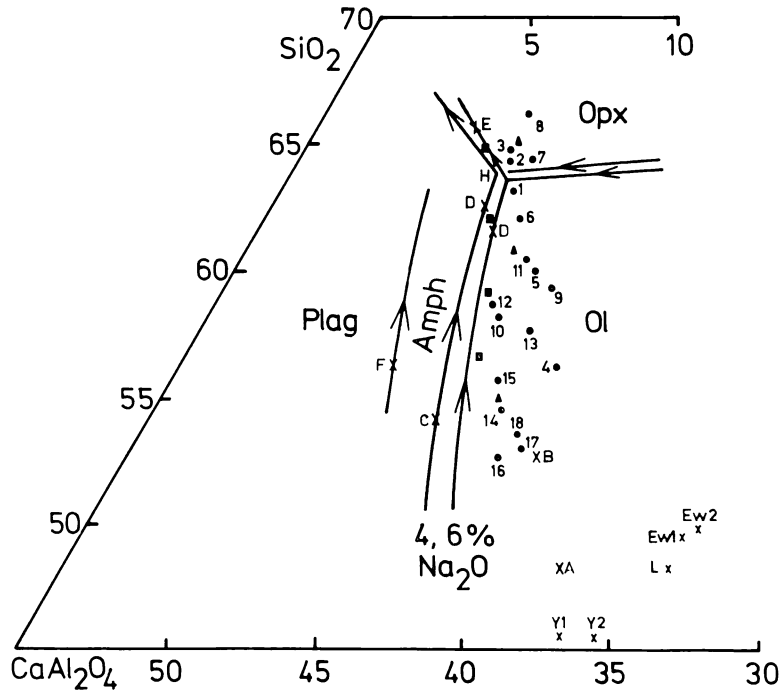


Fig. 5. Weight percent projection from diopside, vapor, and Na_2O into part of the plane CaAl_2O_4 - MgO - SiO_2 . Explanation as for figure 4.

phibole, but that these two minerals coprecipitate in the natural systems. This coprecipitation has also been observed in the simple system CaO - MgO - Al_2O_3 - SiO_2 - Na_2O - H_2O at high alkali contents of the liquids (Cawthorn, in press), but the relations have not been studied in detail.

The various calc-alkaline parental magmas discussed by Best (1969) project close to the olivine-clinopyroxene-amphibole-liquid curve in both diagrams, and hence, although they may have olivine and clinopyroxene as liquidus minerals, amphibole will crystallize at only slightly lower temperatures. Fractional crystallization would be dominated by amphibole precipitation and may produce andesitic liquids (for example, composition E) from these parental magmas.

The three parental magmas of the main provinces of the Japanese archipelago (Kuno, 1967) may have had a crystallization sequence similar to that of B. Analogous basaltic materials studied by Yoder and Tilley (1962) showed such a crystallization history. Hence, they may have ultimately produced andesitic liquids. The alkali contents of these parental magmas range from 1.4 to 4 percent, and hence varying degrees of olivine and clinopyroxene crystallization may be envisaged prior to amphibole precipitation. Hence, removal of varying proportions of amphibole, olivine, and clinopyroxene from these parental compositions will produce slightly different residual liquids.

Using these phase diagrams, it could be argued that partial melting of an amphibole-clinopyroxene-orthopyroxene-olivine rock could produce an andesitic liquid of composition H (see figs. 2 and 3). However, the only way that liquids akin to the parental magmas of the calc-alkaline suite could be produced under these conditions would be if orthopyroxene were the first phase to be consumed and increased melting proceeded along the equilibrium curve olivine-amphibole-clinopyroxene-liquid. Accepted mineral proportions of upper mantle material do not permit such a process. Hence, the concept of fractional melting to produce andesite primary magmas from an upper mantle source is not in accord with the phase equilibria found at 5 kb total pressure. The influence of an increase of pressure to values more likely to be encountered in the uppermost mantle is discussed next.

EFFECT OF VARIABLE TOTAL AND PARTIAL WATER AND OXYGEN PRESSURE

The phase diagrams used in the foregoing discussions were derived from experimental data at 5 kb water pressure. The influence of differing total pressure and partial pressure of water requires examination to determine the physical conditions to which this model may be applied. Yoder and Tilley (1962) examined the phase relationships of natural basalts up to 10 kb water pressure. Their data suggest that the relative stabilities of olivine, pyroxene, and amphibole are comparatively insensitive to pressure changes in the range 2 to 10 kb. The subsequent investigations of Holloway and Burnham (1972) with $P_{H_2O} < P_{total}$ may be interpreted similarly. In these studies the temperature of amphibole entry appears to increase by about 12°C/kb, while olivine and clinopyroxene stabilities remain almost constant. Hence, at pressures higher than 5 kb a slightly larger stability field of amphibole than shown in figures 2 and 3, at the expense of olivine and clinopyroxene, might be anticipated. Similarly, at lower pressures, a smaller amphibole stability field is likely. As an approximation, however, the phase diagrams produced in figures 2 to 5 may be useful in consideration of the character of crystallization sequences in the pressure range 2 to 10 kb.

Green (1973) analyzed amphiboles produced at 10 and 20 kb water pressure; these are similar to the compositions produced at 5 kb and are plotted in figures 2 and 3. Thus crystallization of an amphibole composition, by itself, formed over a range of pressures from basaltic parental liquids may produce a trend toward andesitic liquids.

The stability of amphibole at any particular pressure also depends upon the partial pressure of oxygen (Cawthorn, Curran, and Arculus, 1973; Helz, 1973). The data of Fudali (1965) suggest that the oxygen fugacity of andesites may approximate to the QFM and Ni/NiO buffers at temperatures of about 1000°C (the buffering conditions used by Holloway and Burnham (1972) and Cawthorn, Curran, and Arculus (1973); and, in part, Helz (1973)). Thus the experimental data on natural material carried out with an oxygen fugacity similar to that of andesites are in accord with the phase diagrams derived from the simple system.

Holloway and Burnham (1972) reported that the upper temperature limit of amphibole crystallizing from basic melts may be higher for $P_{\text{H}_2\text{O}} < P_{\text{total}}$ than for $P_{\text{H}_2\text{O}} = P_{\text{total}}$. However, their data also suggest that the upper temperature limits of olivine and clinopyroxene also increase under these conditions relative to the results of Yoder and Tilley (1962). Thus the *relative* stability of minerals does not change with changing partial pressure of water (above $0.5P_{\text{total}}$). Eggler and Burnham (1973) showed that the stability relationships in two natural andesites were sensitive to changes in partial pressure of water at $P_{\text{H}_2\text{O}} < 0.5P_{\text{total}}$ at 5 kb, but at higher partial pressures *relative* mineral stabilities were insensitive to such changes. Hence, although higher temperatures of crystallization are involved with water-undersaturated conditions, the relative stability of phases may not be greatly affected. Since it is the relative stability ranges of phases that govern the form of phase diagrams like figures 2 and 3, these diagrams should apply to water-undersaturated ($P_{\text{H}_2\text{O}} > 0.5P_{\text{total}}$) as well as water-saturated conditions.

Holloway (1973) showed that the maximum thermal stability of synthetic pargasite was sensitive to total pressure and partial pressure of water. The maximum thermal stability at 5 kb occurs for $P_{\text{H}_2\text{O}} = 0.6P_{\text{total}}$ and for $P_{\text{H}_2\text{O}} = 0.4P_{\text{total}}$ at 10 kb. For partial pressures of water below these values, the thermal stability of pargasite decreases rapidly. At 5 kb basaltic and andesitic liquids may dissolve about 8 percent water (Hamilton, Burnham, and Osborn, 1964), and hence to generate a partial water pressure equal to half the total pressure, water contents of about 4 percent would be required. At lower total pressure, lower water contents would be required to stabilize amphibole. Estimation of the actual water content of andesitic lavas is problematic. Chayes (1969) suggested an average value of 1.26 ± 1.08 percent, whereas analyses by Kuno (1969) contain from 0.1 to 5.54 percent water. However, analysis of the water content of a consolidated lava gives no indication of the water content of the original magma. Eggler (1972a) estimated the water content of an andesite from Paricutin by synthesizing the phenocrysts of the lava in experimental runs at various pressures and water contents. The best replication of phenocryst phases was observed when the liquid contained 2.2 percent water. This would appear to be somewhat lower than that required from the above reasoning for amphibole stability if the data of Holloway (1973) for synthetic pargasite are quantitatively applicable to natural magmas, and if the Paricutin lava can be regarded as typical.

DISCUSSION

Amphibole fractionation to produce andesitic compositions was considered by Tilley (1950), but he questioned it as a major process because of the lack of amphibole phenocrysts in lavas. However, as a result of the low-pressure breakdown of amphibole (Boyd, 1959), its rare appearance in andesitic lavas is explicable. In fact, Yoder (1969) states that one of the characteristics of andesite is the presence of amphibole grains in various stages of breakdown.

Best and Mercy (1967) suggested that amphibole fractionation could explain the observed variation in the Guadalupe igneous complex, California. Wager (1962) reported amphibole-rich nodules from the 1902 eruption of Soufrière, St. Vincent, and Lewis (1973) favored the removal of amphibole, clinopyroxene, olivine, and magnetite to produce the chemical variation in the Soufrière volcanics. Murray (1972) interpreted the amphibole-bearing stock-like plugs of Alaska as fractional crystallization products of a calc-alkaline volcanic episode. Amphibole-bearing nodules have been reported from the Japanese archipelago by Aoki (1963, 1970), and Yamazaki, Onuki, and Tiba (1966), and Takeshita (1974) interpreted such inclusions as evidence for the origin of andesitic magmas by fractionation from hydrous basic liquids.

Holloway and Burnham (1972) concluded that the removal of amphibole, olivine, and clinopyroxene from a tholeiitic composition would produce an andesitic liquid, or

“tholeiite” = crystals (amph, cpx, ol) + liquid (andesite).

This geochemical model may be valid irrespective of whether “tholeiite” is a magma or crystalline rock. In other words, if partial melting of oceanic tholeiite (or its metamorphosed equivalent) can produce andesitic liquids, crystallization of tholeiitic magma to give the same residue may also produce the same liquids.

Eggler and Burnham (1973) suggested that amphibole fractionation from andesite may not occur at depths of less than 30 km for the two compositions they studied, as amphibole was not the liquidus phase. However, Allen and Boettcher (1971) presented experimental data where, under 10 kb water pressure, amphibole was observed as the liquidus mineral of an andesitic composition. At lower pressure orthopyroxene and plagioclase crystallized before amphibole. A pressure of 10 kb was also suggested by Cawthorn, Curran, and Arculus (1973) for the crystallization of amphibole from a basanitoid to andesite suite from the Lesser Antilles.

As mentioned earlier, although a pressure of 5 kb was chosen for the experimental study of the simple system, comparison with other data suggests that these phase relationships will be essentially the same over the pressure range 2 kb to at least 10 kb. Hence, a process of amphibole crystallization, either by itself or together with minor olivine and clinopyroxene, from basaltic liquids may produce andesite over a large depth range in the crust and uppermost mantle. The results of Eggler and Burnham (1973) are not, therefore, a serious objection to the general model of amphibole fractionation. While basalts may crystallize any of olivine, clinopyroxene, and amphibole, andesites (with compositions similar to E in figures 2 and 3) are likely to crystallize any of amphibole, orthopyroxene, and plagioclase as a result of the reaction relationship involving olivine and clinopyroxene.

The simple system studied by Cawthorn (in press) did not include iron. As calc-alkaline rocks may be chemically distinguished from tholeiitic rocks by lack of iron-enrichment the exclusion of iron in the simple system requires explanation. Incorporation of iron would intro-

duce two more components (Fe^{2+} and Fe^{3+}) into the system. The volume of data required to define phase relations in an 8-component system would be prohibitive, and diagrammatic representation would be extremely difficult. The partition coefficient of Fe_{total} and Mg between olivine (or pyroxene) and liquid is less than 0.25 and decreases with increasing oxygen fugacity. Hence, fractionation of these phases would produce a noticeable increase in the Fe:Mg ratio in A-F-M (alkali-total iron-magnesia) diagrams. The partition coefficient between amphibole and liquid has been calculated from natural materials to be 0.5 (Cawthorn, in preparation). Hence, removal of such a mineral would produce a relatively slight iron enrichment in A-F-M diagrams. Ringwood (1974) concluded that the Fe:Mg ratio of amphiboles is sufficiently large, compared to olivines and pyroxenes, to be capable of explaining the lack of iron enrichment in calc-alkaline rocks. Hence, we suggest that amphibole fractionation is still capable of producing calc-alkaline trends. To support this assumption we have plotted compositions from the Cascade volcanic suite—a typical calc-alkaline sequence (Carmichael, 1964; Wise, 1969)—on figures 4 and 5. These compositions, which range in SiO_2 from 49 to 62 percent, lie close to the olivine-clinopyroxene-amphibole-liquid curves and project away from plausible amphibole compositions. Their characteristic liquid evolution trends may, therefore, be explained by amphibole-dominated crystallization processes. They describe a trend similar to C-D-E in figures 2 and 3. We suggest, therefore, that these diagrams and the recalculation scheme involved in their construction are suitable for considering the evolution of natural liquids, and that the absence of iron in the simple system is not a serious omission.

High water pressure has been assumed to be a characteristic of calc-alkaline volcanicity (Yoder, 1969). Some calculations on ejecta velocities by Fudali and Melson (1972) implied pressures in excess of 5 kb may be built-up within the superstructure of a volcano. These observations would seem to be excellent supporting evidence for the process of amphibole fractionation. McBirney (1973) suggested that high viscosity of magma might also explain the explosive nature of andesitic volcanoes. However, we repeat Yoder's (1969) observation, that relic hornblende grains are common in andesites, to support our conclusions that calc-alkaline magmas may go through a stage during which amphibole crystallizes.

Basalts are frequently an important component in a calc-alkaline volcanic sequence (Carmichael, Turner, and Verhoogen, 1974; p. 531; McBirney and others, 1974). This is satisfactorily explained by assuming that basalt is the parental magma that undergoes fractional crystallization of amphibole. It does not suffer from the volume problem discussed earlier for magnetite fractionation for two reasons. If fractionation occurs under 10 kb pressure the cumulus hornblende will be left in the upper mantle or base of the continental crust. Hence, the fractionated material need not be spatially closely related to the volcanic sequence. Secondly, the crystallizing hornblende contains approximately 38 to 42 percent SiO_2 . Removal of this phase will cause a rapid enrichment in SiO_2 with a rela-

tively small proportion of crystallization. Hence, a smaller proportion of residue is required by this model than the magnetite fractionation process.

A chemical trend from nepheline–normative to quartz–normative cannot be explained by any anhydrous fractionation process (O'Hara, 1968). Cawthorn, Curran, and Arculus (1973) showed that such a chemical variation, ultimately producing andesitic and rhyolitic compositions, could be explained by amphibole fractionation. Hence, the range of basaltic and andesitic compositions found in orogenic volcanic zones may be explained by amphibole fractionation.

SUMMARY

Simplified basaltic magmas can yield andesite-like residual liquids by amphibole \pm olivine \pm clinopyroxene precipitation accompanied possibly by amphibole + orthopyroxene + plagioclase precipitation from the intermediate compositions. Comparison of the relations in the simple system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-Na}_2\text{O}$ at 5 kb water pressure with melting data on natural material from 2 to 10 kb and with $P_{\text{H}_2\text{O}} < P_{\text{total}}$ suggests that the phase diagrams constructed for the simple system may be used to discuss crystallization of natural material under these conditions. Petrological evidence may be used to support a model for the origin of andesite by amphibole-dominated fractionation of a hydrous basic magma. The association of basalt and andesite is readily explicable by this model, and more specifically the occurrence of orogenic basalts with different compositions, each accompanied by their characteristic type of andesite (McBirney, 1969), is a predictable consequence.

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