PETROGENETIC SIGNIFICANCE OF NORMATIVE CORUNDUM IN CALC–ALKALINE VOLCANIC ROCK SERIES

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The improbability of the high pressure hypothesis of the origin of calc-alkaline acidic magmas is discussed in terms of a CIPW normative composition. Of calc-alkaline volcanic rock series from various localities, unlike of tholeiitic ones, the basalt to rhyolite trend lines intersect a quartz-norite thermal divide; that is, the acidic varieties are C-normative. A fractionation involving amphibole at a moderately high pressure (around 10 kb) under hydrous conditions can explain the intersection. Liquids produced by the direct partial melting of a quartz eclogite or a peridotite would be inevitably Wo-normative at high pressures (>25 kb). Calc-alkaline magmas, particularly of dacite to rhyolite, must suffer chemical modification or initially be formed in the uppermost part of the mantle or in the lower crust.

INTRODUCTION

On the basis of melting experiments, Green & Ringwood (1968) and Green (1972) advocated that an eclogite-controlled fractionation at pressures around 30 kb could derive the magmas of calc-alkaline igneous rock series. This argument was opposed by Stern & Wyllie (1973a), who insisted that the liquids produced in the subducted oceanic crust lay off the basalt-rhyolite join. The difference appears partly due to the insufficient understanding of chemical characters of the natural rocks. It is of petrogenetic significance to know the actual features of variation in the major element chemistry of the well-investigated calc-alkaline volcanic rock series from various localities and to review the chemical relations between liquids formed and crystalline resida in high pressure melting experiments on natural and synthetic rock systems.

The present author will take a critical view of the high pressure origin of calc-alkaline volcanic magmas from a viewpoint of the CIPW normative composition. The norms in mole proportions are calculated after reducing all Fe₂O₃ to FeO to minimize the effect of varying degrees of probable post-eruption oxidation of the analysed samples. Diagrams are constructed in this article by using the mole percentage of the albite in normative plagioclase as abscissa because the plagioclase component becomes albite with the increasing acidity of igneous rock series.

NORMATIVE CORUNDUM, PYROXENE AND PLAGIOCLASE

Calc-alkaline and tholeiitic volcanic rock series

Norms of the calc-alkaline and tholeiitic volcanic rock series are somewhat similar in the basic members, while those in the acidic members are strikingly different from each other (Fig. 1). The calc-alkaline trends vary from basalts with Wo-rich pyroxene component to corundiferous (peraluminous).
Fig. 1. Variation in norms of calc-alkaline and tholeiitic volcanic rock series from various localities. The upper half of the ordinate practically represents the mole percentage of the wollastonite in the normative pyroxene component of rocks concerned here because only a few basic members contain olivine in norm.


The norms, especially of acidic rocks, might be affected seriously by a slight alteration of analysed samples or by a slight technical error (Chayes, 1969). However, the contrast between the two series in Fig. 1 is too systematic to be attributed to these reasonings alone. The peraluminous nature of the acidic members is likely to be an additional yet fundamental character discriminating the calc-alkaline series from the tholeiitic one. Any hypothesis for the origin of calc-alkaline magmas should not avoid the problem of how the peraluminous varieties can be derived, since the actual volcanic rock series, at least cited here, are partly C-normative with no exceptions.

Fig. 2. Compositional relationships in norm among minerals of a simple quartz eclogite assemblage. Q and Ky are tentatively plotted as if they contained normative plagioclase of the same composition as the bulk eclogite though they have no plagioclase component in fact, to demonstrate that their fractionation does not affect the normative plagioclase composition of the resulting liquid.

Abbreviations as in Fig. 1, and Px=clino-orthopyroxene, Q=quartz or coesite, Ga=garnet, Ky=kyanite.

A generalized compositional relationship of normative pyroxene and normative plagioclase components in a simple mineral
assemblage of quartz eclogite is illustrated in Fig. 2. Pyroxene (practically clinopyroxene) is the only phase that can contain a significant amount of Na, in the sense that the most normative albite content of the bulk eclogite is in the pyroxene.

Melting of pyroxene is indispensable to the derivation of Ab-rich liquid from a quartz eclogite, but this process hinders the derivative liquid from decreasing in wollastonite component. The production of an Ab-rich C-normative liquid may be possible if selective solution of the jadeitic component of pyroxene and melting of the peraluminous minerals take place simultaneously. Pyroxene shows small decrease in Na$_2$O content with increasing temperature at high pressures (Kushiro et al., 1972; Green, 1972). However, the clinopyroxenes crystallized at temperatures sufficiently above the solidi (Green & Ringwood, 1968) do not contain the CIPW normative plagioclase more albitic than those of the starting basalts at 27 to 36 kb, which suggests that drastic solution of the jadeitic component of pyroxene is unlikely to be expected just above the solidi. A study on the trace element abundances indicates that kyanite ought to be refractory at low degrees of partial melting of andesite (Gill, 1974). Melting of garnet, required to form a peraluminous liquid, obstructs the liquid from increasing in albite component. The liquid derived through equilibrium partial fusion in the low temperature parts of the melting interval of a quartz eclogite must, thus, be Wo-normative if its plagioclase component is comparatively rich in albite.

Fig. 3 shows the trends in norm of liquids coexistent with up to 35 percent crystalline phase in melting experiments at 27 to 36 kb (Green & Ringwood, 1968; Green, 1972). These experimental results have originally been published as evidences for the propriety of the hypothetical high pressure origin of calc-alkaline magmas. Liquids obtained are not peraluminous, and the liquid lines often make high angles with the natural trends. With few exceptions, there can be found a general tendency that the normative pyroxene and normative plagioclase in the liquid increase wollastonite and albite components respectively in concord with the increasing crystallization. These features show that the liquids produced in the upper parts of the crystallization interval at 27 to 36 kb by equilibrium crystallization of basaltic to andesitic melt do not follow the natural calc-alkaline trend. Equilibrium crystallization is the exact reverse of equilibrium partial fusion, so that the above considerations indicate that the natural calc-alkaline trends cannot be the products of any equilibrium process at high pressures.

An incipient liquid produced through fractional partial fusion of a quartz eclogite
cannot be peraluminous since this liquid is similar to the first liquid formed through equilibrium partial fusion (Stem & Wyllie, 1973a). An assemblage of the residual minerals remains eclogitic in a general sense at a time of low degrees of partial melting, though quartz (or coesite), kyanite or both might be absent. Pyroxene at the second stage of fractional fusion must be less jadeitic than that in the original quartz eclogite because of the higher temperature. A liquid produced would, therefore, contain less albitic normative plagioclase in a later stage than in an earlier stage. Consequently, it seems that the incipient liquid is the most sodic of all derived from a quartz eclogite through fractional partial fusion but that this liquid is Wo-rich pyroxene-normative, discording with the known characteristics of the calc-alkaline dacite and rhyolite.

Data for the liquidus phase relations experimentally determined at 27 to 36 kb on synthetic and natural rock systems in connection with the genesis of calc-alkaline magmas are collected and illustrated in Fig. 4 as a function of the normative composition. Peraluminous minerals, such as garnet, kyanite and/or corundum, are the liquidus or near liquidus phase in relatively

Fig. 4. Liquidus and near liquidus phase relationships of rock systems in connection with the calc-alkaline magma genesis at 27–36 kb as a function of normative composition.

The right hand figure is for runs probably containing H2O more than 5% though some experiments cited are conducted with unknown amounts of H2O.

Abbreviations as in Fig. 1, and the near liquidus minerals: open circles = clinopyroxene; solid circles = peraluminous minerals (garnet, corundum and/or kyanite) with or without quartz or coesite; crosses = clinopyroxene plus garnet, or being variable with varying H2O content of the system; light lines = calc-alkaline trends superimposed from Fig. 1.

Data sources: 1 = Green & Ringwood (1968); 2 = Green & Ringwood (1972); 3 = Green (1969); 4 = Green (1972); 5 = Khitarov et al. (1972); 6 = Huang & Wyllie (1973); 7 = Stem & Wyllie (1973a), with chemical data for the gabbro and the red clay from Lambert & Wyllie (1970) and Ronov & Yaroshovsky (1969) respectively because of the insufficient information of chemistry in the original article; 8 = Stem & Wyllie (1973b); 9 = Lambert & Wyllie (1974); 10 = Nicholls & Ringwood (1973).
Wo-poor or C-bearing systems, regardless of H₂O content, with a single exception of a biotite granite (8 in Fig. 4), in which pyroxene appears prior to kyanite under less hydrous conditions. Consequently, it is indicated that fractional crystallization of Wo-normative basalt magma cannot yield C-normative andesitic to rhyolitic magmas at high pressures. This is in essential agreement with the rapid expansion of primary phase volume of garnet in the mafic and ultramafic systems at 30 kb and above (O'Hara, 1968).

DISCUSSION

Neither partial melting nor partial crystallization with an eclogitic residuum is likely to produce any peraluminous liquid from a basaltic parent, as described above. Basalts of various chemistry are inverted mineralogically to eclogite on the solidi at pressures between 18 and 24 kb under anhydrous conditions (Yoder & Tilley, 1962; Cohen et al., 1967; Green & Ringwood, 1967a) and at 25 kb under H₂O-saturated conditions (Lambert & Wyllie, 1972). Thus, it can be said that the calc-alkaline C-normative magma would not be derived at 25 kb and above. Stern & Wyllie's (1973a) statement that the partial melting of the oceanic crust does not produce the calc-alkaline magmas intermediate and acidic at high pressures is confirmed in this article in terms of the CIPW norms.

Discussions are going on about the possibility of the hydrous peridotite origin of an andesite magma (e.g. Mysen et al., 1974). The mineral assemblage of peridotite can be illustrated in a diagram similar to Fig. 2: bulk peridotite, olivine and spinel are in place of the Bulk eclogite, Q and Ky in Fig. 2 respectively. Again pyroxene is the only phase that contains a significant amount of Na. The hypothesis of the hydrous peridotite origin of the calc-alkaline magmas would, thus, be met by the same kind of difficulty at high pressures as is the hypothesis of the eclogite-controlled fractionation, even if SiO₂-rich liquids could be formed.

One probable mechanism for the production of a peraluminous magma is a fractionation of abundant calcic amphibole. This view is supported experimentally by Green & Ringwood (1968) and Holloway & Burnham (1972). Green & Ringwood (Table 28, 1968) showed that the liquid fraction contains more normative corundum with increasing crystallization of amphibole in their 9–10 kb runs. Holloway & Burnham (Table 8, 1972) showed that a crystalline phase including amphibole was in equilibrium with C-normative liquid, while one excluding amphibole coexisted with Wo-normative one at 5 to 8 kb. The amphibole-controlled fractionation hypothesis would be applicable at least between 5 and 15 kb because the fractionation of a hydrous andesite magma involves mainly amphibole in this pressure interval (Green, 1972).

Another mechanism explaining the generation of a peraluminous magma, i.e. the fractional crystallization involving effective removal of clinopyroxene under hydrous 10 kb condition, has been demonstrated by Kushiro & Yoder (1972) according to the melting experiments on the system CaO-MgO-Al₂O₃-SiO₂-H₂O. C-normative liquids have been obtained with crystalline residua composed of plagioclase and pyroxene from an andesite at 9 to 13.5 kb by Green (Table 9, 1969). However, the Green’s (1969) liquid becomes enriched in iron with increasing SiO₂ content. Oxide
minerals, which must be precipitated with anhydrous silicates for the derivation of a no-iron concentration trend, are unstable at the liquidus of andesite melt under the natural geologic conditions (Eggler & Burnham, 1973). Consequently, the calc-alkaline peraluminous magma would not be a product of the effective fractionation of clinopyroxene.

The above-mentioned experimental results by Kushiro & Yoder (1972) and Green (1969) indicate that the quartz-norite divide (O'Hara, 1968) does not persist under the experimental conditions. A Wo-normative magma derived from a quartz eclogite of the oceanic crust and an acidic C-normative magma derived from oceanic silicous sediments may, therefore, be capable of blending in the lower crust or the uppermost mantle to produce a series of calc-alkaline magmas.

$K_2O$ may be concentrated into an ascending magma by the wall-rock reaction (Green & Ringwood, 1967b). If this is the case, $Al_2O_3$ in excess of alkali decreases in amount, resulting in the concomitant increase of wollastonite in pyroxenic component of the magma. A shallower site of origin is preferable for the derivation of a peraluminous magma, because the longer the distance through which the magma has to pass, the higher the $K_2O$ enrichment may be.

The apparent correlation between $K_2O$ content of andesite volcano and depth of seismic zone beneath the volcano (Hatherton & Dickinson, 1969) may suggest the deeper origin of the andesite magma. However, the correlation coefficient of normative composition with depth of earthquake foci becomes worse with increasing acidity of rocks (Sugimura, 1973). Modification in chemistry of calc-alkaline magmas initially formed in the depth may, thus, have occurred at shallower levels.

Although mechanisms such as the assimilation of crustal materials (e.g. Kuno, 1950), the volatile transfer of alkali elements (Kuno, 1968) and the crustal fusion (Ewart & Stipp, 1968; Pichler & Zeil, 1972) might be applicable to the petrogenesis of calc-alkaline peraluminous magmas, they are not operative in the mantle.

In summary it appears difficult to escape the conclusion that no liquid derived from a basaltic parent at high pressures (>25 kb) contains normative corundum, and that, for this reason, most calc-alkaline magmas of intermediate to acidic compositions must have suffered modification, or initially been generated, at moderately high pressures (around 10 kb). In any case, the discussions above do not conflict with geophysical observations. Based on gravity anomalies, Yoshii (1972) proposed a crust-mantle model that the low $Q$, $V$, $p$ zone, where interstitial liquid may exist (Lambert & Wyllie, 1970), comes in direct contact with the crust beneath an island arc around northeastern Japan.

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