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Significance of hornblende in calc-alkaline andesites and basalts

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Abstract

Hornblende occurs in some andesitic and basaltic rocks of calc-alkaline affinity, where it is commonly associated with olivine. The texture, eruption history, and composition are interpreted to indicate that hornblende commonly forms as a product of reaction between olivine and basaltic and andesitic liquids. The natural hornblendes probably formed within the crust at temperatures between 960° and 1080°C from liquids with less than about 6 weight percent H_2O. The formation of hornblende from basaltic liquid within the crust has implications for evolution of continental crust, as well as for the origin of andesite and thermal conditions in subduction zones.

Introduction

Boettcher (1973) and others (Mueller, 1969; Holloway and Burnham, 1972; Green, 1972; Helz, 1976; Cawthorn and O'Hara, 1976; Allen and Boettcher, 1978) argue that amphibole plays an important role in governing the compositions of calc-alkaline andesites. The mechanisms whereby amphibole supposedly exerts its role are not clear. Is it left behind in a crystalline residue—where is it: in the crust or in the mantle? Does amphibole crystallize and separate from a parental liquid—what are the composition and temperature of the parental liquid? Does amphibole crystallize from a derivative liquid which mixes with a parental liquid to yield andesite? Amphibole occurs in some calc-alkaline volcanic and plutonic rocks with basaltic and andesitic bulk compositions, but the significance of such occurrences is uncertain without textural evidence of how it got there: is the amphibole a primary igneous mineral or a product of alteration? If igneous, over what interval of crystallization did it form, and was the composition of the liquid in that interval andesitic, dacitic, or basaltic? If amphibole can be shown to have actually formed from a liquid with a certain composition, what does that portend for the concentration of H_2O in and the temperature of the liquid? My aim is to help point the way to answers to some of the above questions by critically examining evidence on the growth of amphibole from basaltic and andesitic liquids, both experimental and natural.

Definitions

In using the word liquid, I mean to refer to a single state of matter (a homogeneous liquid phase). It is vital to distinguish between the composition of a liquid (generally a residual liquid) and the composition of the bulk material. Petrographically a certain hornblende may be associated with a particular residual liquid. Experimentally a certain bulk composition may crystallize hornblende at or below the liquidus. The residual liquid associated with hornblende will generally differ in composition from the bulk. Thermodynamically the composition and temperature of a certain liquid can remain constant as the proportions of crystals and liquid vary. To interpret a given association of hornblende and liquid, the petrographer must seek experimental conditions which yield hornblende and liquid with compositions similar to those observed. If analogy is drawn with a particular bulk composition (and liquidus hornblende) the implied pressure (and concentration of H_2O in the liquid) is larger than if analogy is made with a residual liquid. The implications for temperature are complex and depend on the concentration of H_2O in the liquid as well as on compositional features such as Fe/Mg and concentrations of alkalis.

Hornblende in experimental products

Experimental studies yielding hornblende in products with either calc-alkaline bulk compositions or with residual liquids having analogous compositions

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reveal: (1) Hornblende is a liquidus or near-liquidus mineral in some basaltic bulk compositions if P_{H_2O} exceeds about 10 kbar (Yoder and Tilley, 1962; Green and Ringwood, 1968; Allen *et al.,* 1975; Stern *et al.,* 1975) and if H_2O dissolved in liquid exceeds about 12 weight percent. (2) In some andesitic bulk compositions hornblende is a liquidus mineral if P_{H_2O} exceeds about 2 kbar (Piwinskii, 1973). (3) As P_{H_2O} decreases below P_{total}, the hornblende-out curve lies progressively farther below the liquidus (Robertson and Wyllie, 1971; Holloway and Burnham, 1972; Green, 1972; Eggler and Burnham, 1973; Allen and Boettcher, 1978). (4) The proportion and composition of residual liquid change dramatically over an interval of temperature less than 50°C after the beginning of crystallization of hornblende (Holloway and Burnham, 1972). (5) Near the liquidus low oxygen fugacity favors the crystallization of hornblende compared to pyroxene (Helz, 1973, 1976). (6) The reactions between hornblende, liquid and other crystals are complex (Bowen, 1928, p. 61, 85, 111; Helz, 1976). (7) Hornblende is stable to the highest temperatures and lowest concentrations of H_2O in liquid in systems (a) where olivine is present (Helz, 1976), (b) where $P_{H_2O} < P_{total}$ (Holloway, 1973), and (c) where significant F is present (Holloway and Ford, 1975).

The above relations are summarized on Figure 1. The coordinates of Figure 1 are qualitative. Quantitative values will vary with bulk composition. Lesser MgO and Mg/(Fe+Mg) will diminish the temperature of olivine, pyroxene, and hornblende liquidus surfaces. The field for liquidus hornblende will then extend farther into the vapor-absent portion of the diagram. Lesser concentrations of Al_2O_3 will shift more of the liquidus surface into the olivine and pyroxene fields and diminish the area of the liquidus field for plagioclase. Consequently, the combination of low Al_2O_3 and high MgO may obliterate the liquidus surface having hornblende, olivine, and plagioclase (see Bowen, 1928, p. 111). For a natural magma with CO_2 as well as H_2O, there will be a range in X_{H_2O} in addition to a boundary marking vapor-absent and vapor-present regions. Reactions between olivine, pyroxene, hornblende, and liquid add complications not shown on the diagram. Spinel and magnetite are probable additional liquidus minerals but are not shown. For simplicity only one pyroxene is depicted. Calcium-rich clinopyroxene is the liquidus pyroxene but is joined and/or replaced by orthopyroxene below the liquidus at temperatures below or near that of the appearance of hornblende. Except for such simplifications, the diagram is consistent with existing experimental and natural data.

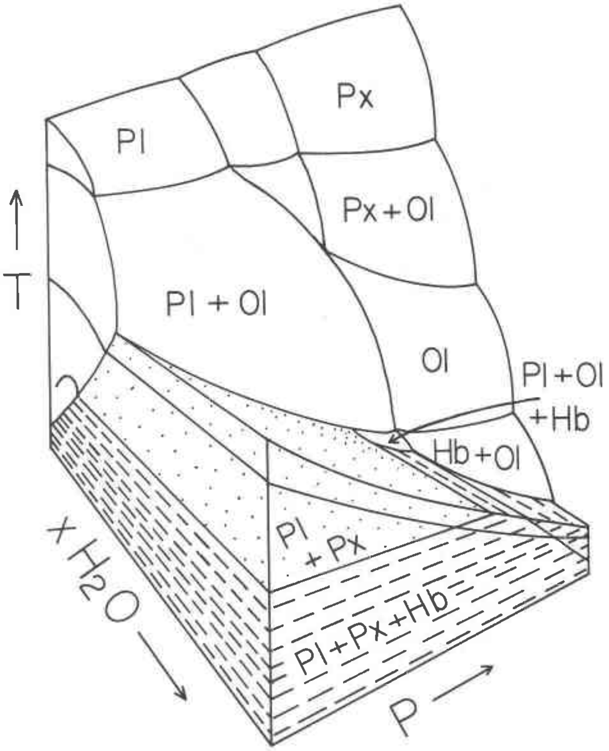

Fig. 1. Simplified hypothetical P–T–X_{H_2O} equilibrium diagram for a high-alumina basalt. The diagram is drawn in perspective. The origin is not shown. The concentration of H_2O refers to the bulk material. The stippled and dashed regions are saturated with vapor rich in H_2O. Below the liquidus surface the pyroxene (Px)-out and olivine (Ol)-in surfaces are assumed to coincide for simplicity. Fields for spinel and magnetite are omitted for simplicity. Hornblende (Hb) is a liquidus mineral in both vapor-absent and vapor-present regions. The liquidus hornblende is accompanied either by liquidus Ol or by both plagioclase (Pl) and Ol. Only one symbol is shown for pyroxene (Px). Liquidus Px is calcium-rich. Low-calcium pyroxene probably predominates if Hb is abundant.

It would be helpful to know the positions of surfaces of equal SiO_2 in the liquid (H_2O-free basis). At present the coordinates of such surfaces in Figure 1 are uncertain. Qualitatively, it is possible to give some limits. I consider a surface of SiO_2 = 60 weight percent on an anhydrous basis, corresponding roughly to andesite. Because the composition of the residual liquid changes steeply with temperature after the beginning of crystallization of hornblende (Holloway and Burnham, 1972), it is reasonable to expect the 60 percent SiO_2 surface to lie close to the hornblende-out surface. In the region of the diagram where hornblende is a liquidus mineral (hornblende-out corresponds to liquidus), the 60 percent SiO_2 surface must lie below the hornblende-out surface. In the region of the diagram where the hornblende-out surface is far below the liquidus (for example, subaerial basalts with about 0.1 weight percent H_2O), residual liquids with more than 60 percent SiO_2 may develop in the absence of hornblende. Therefore, the 60 percent SiO_2 surface may intersect the hornblende-out surface, unless crystallization intervenes.

It is probable, but uncertain, that residual liquid in anhydrous high-alumina basalt attains 60 percent SiO_2 before complete crystallization if equilibrium is maintained. Residual glasses in natural high-alumina basalts have 62 (Fuego volcano, Guatemala—Rose *et al.,* 1978) and 67 (Hat Creek flow, California—Anderson and Gottfried, 1971) percent SiO_2. However, equilibrium is not maintained throughout the natural rocks. Because the minerals [plagioclase (An55), augite, olivine (Fo66), and magnetite] associated with the residual glass at Fuego are compositionally similar to the normative minerals [plagioclase (An50), pyroxene, olivine (Fo70), magnetite, and ilmenite, based on the weighted average composition with 1/3 of the iron trivalent], I conclude that anhydrous, calc-alkaline, high-alumina olivine tholeiites exemplified by Fuego probably yield equilibrium residual liquids with 60 percent or more SiO_2 before complete crystallization. Therefore the equilibrium surface for residual liquids with 60 percent SiO_2 probably intersects the hornblende-out surface.

The intersection of the 60 percent SiO_2 and hornblende-out surfaces may have major petrological significance. In a given bulk composition residual liquids with 60 percent SiO_2 will vary compositionally in accordance with the amounts of associated minerals, particularly hornblende. Many workers have pointed out that crystallization of hornblende can yield calc-alkaline residual liquids (Green and Ringwood, 1968; Boettcher, 1973; Holloway and Burnham, 1972; Helz, 1976; Cawthorn and O'Hara, 1976). Andesitic residual liquids not associated with hornblende may be alkalic or alkali-calcic. The residual liquid with 60 percent SiO_2 may have both a smaller ratio of Fe/(Mg+Fe) and a lower temperature if hornblende is present than if it is absent. For a given bulk composition the amount of hornblende associated with a residual liquid having 60 percent SiO_2 will be maximized: (1) if the initial concentration of H_2O is large; (2) if crystallization occurs at constant or increasing pressure; and (3) if equilibrium (reaction) is maintained. Consequently, many differences between various andesitic liquids may be explained by either contrasting initial concentrations of H_2O in parental high-alumina basaltic magma, variable depth of crystallization, or extent of reaction during crystallization.

Some natural calc-alkaline liquids associated with hornblende are less siliceous and hotter than most experimental analogs. The natural occurrences suggest that the field of liquidus hornblende extends to lower concentrations and partial pressures of H_2O than is indicated by most existing experimental results.

Hornblende associated with natural andesitic liquid

Many andesites have phenocrysts of hornblende (see for example, Moorhouse, 1959, p. 189–190; Turner and Verhoogen, 1960, p. 272–282) but most do not. Many, perhaps most, andesites contain clots of anhydrous crystals which may be reaction products of hornblende (Stewart, 1975); however, the occurrence of oscillatory zoned plagioclases within such clots suggests a different origin (Garcia and Jacobson, 1979).

Most hornblende andesites have more than about 60 percent SiO_2 (Kuno, 1950; Jakěs and White, 1972; Sakuyama, 1979); the groundmass probably is dacitic to rhyolitic in composition. The hornblendes commonly are rimmed or cored by crystals of pyroxene, plagioclase, and other minerals. The compositions of the hornblendes may be modified after crystallization. Thus the compositional relations between hornblende and andesitic liquid are difficult to infer from most occurrences.

Below I describe an association of hornblende and andesitic glass included in olivine from a lapillus of porphyritic andesite.

The 1783 eruption of Asama Volcano, Japan. Background: the eruption and its products

Asama volcano is a composite andesitic stratovolcano in central Honshu, Japan. Its geology is documented by Aramaki (1963) and briefly summarized by Anderson (1979).

The history of the 1783 eruption helps constrain the history of cooling and decompression which affected the extruded products. Although complex, this eruption probably is typical of the principal way Asama has grown. It involved a succession of Plinian explosions which produced about 0.17 km^3 of pyroclastic material (Minakami, 1942) and an equal volume of lava (Aramaki, 1956). The early products were air-fall pumice lapilli and ash; ash flows formed on and after August 3 when the culminating blast occurred; an andesitic lava flow formed during the final phase of the eruption. The details are reported by Aramaki (1956, 1957), who interpreted the eruption sequence in terms of an initial vent-clearing phase between June 25 and August 2, 1783 followed by extrusion from a subvolcanic body of magma on and after August 3, 1783.

Petrography. The 1783 andesitic pumice lumps vary from light to medium brown; some have streaks of different shades of brown. Lapillus AM2-2 (Anderson, 1979) is medium brown. It was collected from a layer of air-fall lapilli which probably formed on or before August 2.

The pumice contains mm-sized phenocrysts of plagioclase, augite, hypersthene, magnetite, and ilmenite. Plagioclase is the principal phenocryst and makes up about 20 volume percent of the pumice on a void-free basis. Most of the plagioclases are subhedral to anhedral crystals with irregular cores sieved with vermicular inclusions of glass and gas. The cores are surrounded by a normally-zoned rim which is free of inclusions and 10 to 50 μm thick. Other plagioclases are poor in inclusions and oscillatory-zoned with skeletal protrusions. The augites contain inclusions of glass and lamellae of pyroxene in irregular, pale green cores. Some augites occur in clots where they are subhedral and irregular against each other. Commonly a zone of inclusions of plagioclase and pyroxene marks the boundary between a pale green core and deeper green rim. The rims are 50 to about 150 μm thick. Glasses included in pyroxene, plagioclase, and oxide phenocrysts range from about 70 to 79 weight percent SiO_2; the host glass outside of the phenocrysts has about 72 percent SiO_2 (Anderson, 1979).

Crystals of olivine (Fo79–Fo85) are rare. The olivines have 50-μm-thick rims of hypersthene or augite. There is more olivine in medium-brown pumice than in light brown pumice. Inclusions of glass in olivine crystals have 54 to 61 weight percent SiO_2 on an anhydrous basis (Anderson, 1979).

Hornblende associated with andesitic glass. Hornblende occurs together with andesitic glass included in an olivine crystal from the lapillus AM2-2 of medium-brown andesitic pumice (Fig. 2, Table 1). The hornblende is pale brown and faceted against glass. A second mineral (probably orthopyroxene) occurs with hornblende in the inclusion. It is colorless, long and prismatic, and has a refractive index close to that of the hornblende. The included glass has a round contact with the olivine host crystal. The microprobe analysis yields an estimated 4 percent of H_2O in the glass (Anderson, 1979).

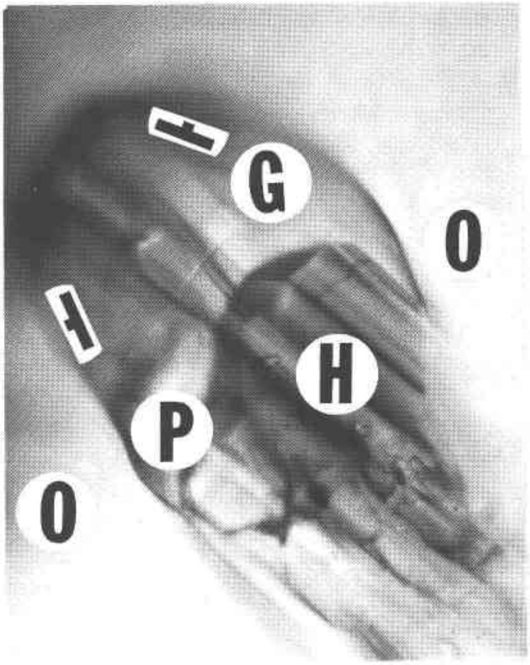

Fig. 2. Inclusion of glass (G), hornblende (H), and probable pyroxene (P) in olivine (O). The long dimension of the photograph is about 200 μm. Dip and strike symbols refer to the attitude of the contact between olivine and glass referred to the polished surface as horizontal. The olivine crystal is rimmed by orthopyroxene and is from a lump of pumice extruded from Asama volcano, probably on or before August 2, 1783.

A second, smaller inclusion in the same olivine crystal contains a pale brown crystal which is probably hornblende (Fig. 3). It comprises about 2 volume percent of the inclusion. Anisotropic and opaque crystals line the inside wall of the vapor bubble in the small inclusion.

The olivine host crystal of the hornblende-bearing inclusion is Fo83 (Table 1) compared to Fo79 to Fo85 for olivines from other lumps of pumice of the 1783 eruption (Anderson, 1979). The composition of the preserved glass (Table 1, column 2) is close to but more silicic than that of other inclusions in olivine which lack hornblende (Table 1, column 4).

Hornblende comprises about 30 volume percent of the large inclusion (Fig. 2), some of which was removed by sectioning. Probable orthopyroxene comprises about 10 volume percent. Most inclusions in Asama olivines are subspherical to ellipsoidal. The hornblende-bearing inclusion has walls which dip away from the inclusions at high angles (Fig. 2).

Attached phenocrysts of magnetite and ilmenite occur in the same lump of pumice. Their composi-

Table 1. Chemical compositions of hornblende and andesitic liquid with comparisons

Col.[1]	1	2	3	4	5	6	7	8	9
SiO_2	42.6	61.3	57.0	56.0	60.5	55.5	63.2	63.8	60.0
Al_2O_3	15.5	21.0	20.9	19.7	20.0	17.3	20.3	18.6	20.4
FeO[2]	8.2	3.4	3.6	6.9	4.2	8.5	3.0	4.3	4.5
MgO	15.6	2.6	3.4	3.0	1.1	3.4	0.3	0.7	4.3
CaO	12.7	5.5	8.9	10.0	8.4	9.2	7.4	6.9	7.5
Na_2O	2.6	4.3	4.0	2.9	3.2	2.8	3.0	2.8	0.9
K_2O	0.3	1.5	1.2	0.6	0.8	0.7	0.9	1.0	0.9
TiO_2	2.4	0.3	1.2	0.8	1.3	2.2	1.2	1.2	1.2
Cl	0.05	0.15	0.12	0.08	n.d.	n.d.	n.d.	n.d.	n.d.
Sum[3]	98.2	97.4		95.5	87.3	85.7	84.0	83.7	n.r.
H_2O[4]	3	4		3	10	10	10	6	?10
T[5]	1080-960	1080-960		1080-960	1015	1045	1050	999	1010
P[6]	0.1-1?	0.1-1?		0.1-1?	5	5	8.0	5.2	13
Assoc.[7]	Fo83,Px?	Hb,Fo83, Px?		Fo79	Hb,Cpx, Ol	Hb,Cpx, Ol,Ox	Hb,Cpx, Ol,Mt	Cpx,Hb, Ol,Mt	Hb,Cpx Ox

[1] See key to columns below.

[2] All iron as FeO.

[3] Sum of the original analysis. Reported analyses are recalculated to 100 percent except for rounding errors. Original sum for column 9 is not published. Sums are H_2O-free.

[4] Estimated concentration of H_2O. Estimated by difference (Anderson, 1973) for columns 1, 2, 4; estimated from pressure, gas composition and solubility otherwise.

[5] Estimated temperature in degrees Celsius. See text for columns 1, 2, 4. Otherwise published run temperature.

[6] Estimated pressure in Kbar. See text for 1 and 2. Otherwise run pressure (total pressure not necessarily same as P_{H_2O}).

[7] Coexisting minerals: Fo = olivine with atomic ratio of 100 Mg/(Mg+Fe); Hb = hornblende, Px = pyroxene, Cpx = calcium-rich pyroxene, Ol = olivine, Mt = magnetite, Ox = oxide.

Key to Columns:

1 = Hornblende included in olivine together with glass of column 2 (analysis 9 of Table 3 of Anderson, 1979).

2 = Andesitic glass included in olivine, Asama 1783 (analysis 8 of Table 3 of Anderson, 1979).

3 = Result of adding 0.4 parts hornblende (column 1), 0.7 parts glass (column 2), and 0.1 part of orthopyroxene (stoichiometric En83) and subtracting 0.2 parts olivine (Fo83).

4 = Andesitic glass included in olivine, Asama 1783 (analysis 10 of Table 3 of Anderson, 1979).

5 = Synthetic andesitic glass (analysis 15a of Table 7b of Helz, 1976).

6 = Synthetic andesitic glass (analysis 16a of Table 7b of Helz, 1976).

7 = Synthetic andesitic glass (from Table 8 of Holloway and Burnham, 1972).

8 = Synthetic andesitic glass (from Table 8 of Holloway and Burnham, 1972).

9 = Synthetic andesitic glass (average of analyses 21 and 22 of Table 6a of Allen and Boettcher, 1978).

tions (Hm24, Usp34) suggest a temperature of equilibration of 1080°C, according to the unpublished geothermometer of Lindsley and Rumble (1977). The same compositions suggest a temperature of 1060° to 1070°C, according to my visual interpolation of data by Buddington and Lindsley (1964) and Taylor (1964). Similar compositions but lower temperatures (990°–1020°C) were reported by Oshima (1976).

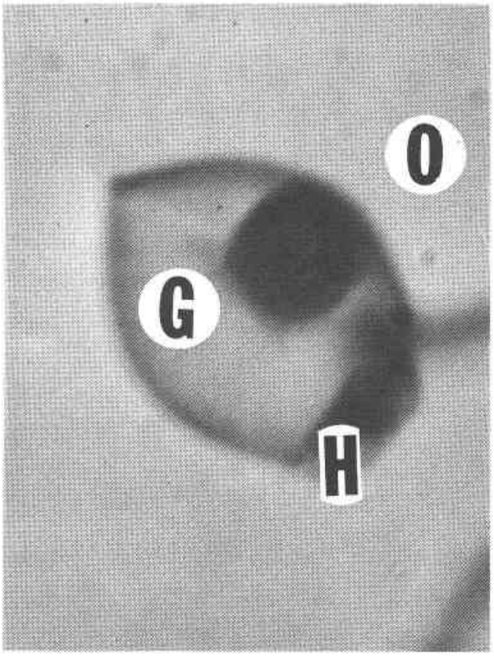

Fig. 3. Photograph of a second, smaller inclusion in the same crystal as that shown in Fig. 2. The inclusion is about 30 μm long and contains a pale brown crystal of probable hornblende (H) and a dark bubble of vapor.

Interpretation

The andesitic glass (Table 2, column 1) probably is in a state of quenched equilibrium with olivine (about Fo83) and hornblende, because the pumice lump in which it occurs was explosively erupted and cooled in air before falling to the ground. The inclusion probably cooled from about 1080°C to a few hundred degrees C in a few minutes, judging from the Plinian explosions which probably erupted it in late July or early August of 1783 (Aramaki, 1956; written communication, 1979). Possibly the inclusion was contained in a froth of magma at a few hundred atmospheres or less for a few days, because it was extruded during the early part of the eruption when the vent probably was intermittently filled with froth.

I interpret the textural, compositional, and historical facts to suggest that andesitic or basaltic liquid carried crystals of olivine into a crystal-rich body of andesitic magma during or before the early stages of the eruption (May 9 to August 2). The irregular anhedral cores of many plagioclase crystals suggest fragmentation. The abundance of gas in the sieved cores suggests that fragmentation was accompanied by and/or caused by effervescence. The rims on the crystals of plagioclase, pyroxene, and olivine indicate that reaction and crystallization took place after fragmentation. The faceted (not skeletal) shape and size of hornblende included in olivine suggest it to be a daughter crystal or reaction product rather than a quench crystal or product of devitrification. The round contact between the olivine and glass associated with hornblende is consistent with a reaction relation between olivine, liquid, and hornblende. Crystals intergrown with a residual rhyolitic liquid were broken apart and overgrown probably because invading, olivine–porphyritic magma caused effervescence of the interstitial liquid (due to pressure release and/or temperature increase) and contaminated the liquid with relatively refractory constituents.

Liquids trapped within the olivine crystals became modified in composition as a result of growth of daughter crystals of hornblende and/or pyroxene and reaction with olivine, because the temperature decreased from that in the initial environment to near that of the invaded andesitic magma with residual rhyolitic liquid.

The initial composition of the trapped liquid before crystallization of hornblende and pyroxene can be estimated by adding 0.4 parts hornblende, 0.1 parts pyroxene and 0.7 parts andesitic glass, and subtracting 0.2 parts olivine. The result (Table 1, column 3) is somewhat similar in composition to other inclusions of andesitic glass in olivines which lack hornblende (Table 1, column 4). If other minerals are included in the calculation, the similarity can be increased. Some inclusions of glass in the Asama 1783 olivines have as little as 54 percent SiO_2 (Anderson, 1979). It is not possible to relate all the glasses to a common precursor without including either minerals not now in contact with the glasses, or residual rhyolitic liquids as mixing components, or both. The origins of the glasses included in the olivines are complex if considered in detail. Such detail is beyond the scope of this paper. Subtraction of olivine in the above calculation corresponds to resorption of olivine concomitant with crystallization of hornblende and pyroxene from a less silicic liquid precursor. Probably the andesitic liquid was in equilibrium with hornblende, pyroxene, and olivine at the temperature of eruptive quenching; however, the relation with olivine probably was one of reaction.

Two kinds of experimental results can be compared with the natural association of hornblende, pyroxene, olivine, and andesitic liquid. Consequently, it is possible to obtain two estimates of the temperature and the concentration of H_2O in the silicate liquid. In the first case comparison is made with the liquidus

Table 2. Chemical compositions of hornblendes and associated basaltic materials

Col.[1]	1	2	3	4	5	6	7	8	9
SiO_2	42.8	54.5	51.0	42.1	51.7	41.4	54.0	40.7	55.5
Al_2O_3	13.6	18.1	19.1	14.3	18.4	16.5	17.7	13.3	17.3
FeO[2]	10.5	9.4	10.0	10.8	9.7	12.4	9.2	14.2	8.5
MgO	15.3	3.5	5.4	15.6	5.3	14.1	4.8	13.0	3.4
CaO	12.2	8.3	9.3	11.8	10.3	11.0	8.3	10.7	9.3
Na_2O	2.3	3.7	3.0	2.5	2.9	2.6	3.8	2.0	2.8
K_2O	0.4	1.0	0.6	0.3	0.5	0.1	0.8	0.5	0.7
TiO_2	2.7	1.2	1.1	2.1	1.0	1.8	1.3	4.4	2.2
Cl	0.05	0.12	0.09	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sum[3]	98.9	93.8	94.3	99.8	99.8	98.7	99.8	98.7	85.7
H_2O[4]	1	4	4	1.8	n.d.	n.d.	n.d.	n.d.	8
T[5]	1030	1030	1030	n.d.	n.d.	1000	1000	1045	1045
P[6]	1-2	1-2	1-2	8	8	12-30	12-30	5	5
Assoc.[7]	An92	An86	Fo79	Ol,Cpx, Pl,Mt	Ol,Cpx Hb,Pl, Mt	Fo83	Ol,Pl	Fo82-84 Cr,Cpx	Fo82-84 Hb,Cr,Cpx

Key to Columns (see Table 1 for footnotes):

1 = Hornblende included in core of plagioclase phenocryst from Fuego (analysis reported in legend to Figure 16, p. 20 of Rose et al., 1978).

2 = Glass included in rim of plagioclase phenocryst (An83) of column 7 (analysis No. 6 of Table 6 of Rose et al., 1978).

3 = Glass included in olivine (Fo79) from Fuego (analysis 4 of Table 6 of Rose et al., 1978, and close in composition to the weighted average of the 1974 erupted ash).

4 = Hornblende from gabbroic block, La Soufrière, St. Vincent (analysis 1 of Table 6 of Lewis, 1973a).

5 = Fine grained, interstitial material from same gabbroic block as column 9 (analysis 1 of Table 4 of Lewis, 1973b).

6 = Hornblende inclusions in olivine phenocrysts, Little Mt. Hoffman basalt, California (column 2, Table 2 of Mertzman, 1978).

7 = Groundmass of Little Mt. Hoffman basalt (calculated by subtracting 10 percent olivine [Fo80] and 25 percent plagioclase [An70] from the bulk rock--analysis 1 of Table 1 of Mertzman, 1978).

8 = Synthetic hornblende (Helz, 1976, Table 13a, No. 2, p. 192).

9 = Synthetic liquid associated with hornblende (column 8) calculated by Helz (1976, Table 7b, analysis No. 16a, p. 152).

phases of an andesitic bulk composition. In the second case comparison is made with the residual liquid in a basaltic bulk composition.

For the first comparison two assumptions are necessary: (1) the hornblende is a hydroxy-hornblende; (2) the minerals in contact with the natural andesitic liquid are thermodynamically equivalent to the liquidus phases of a system composed of the liquid alone.

The first assumption is justifiable because: (1) the natural hornblende contains negligible chlorine; (2) its pale color suggests a negligible concentration of oxycomponent; and (3) its fluorine content is unknown, but probably small, because fluorine is a minor constitutent of most magmas. The second assumption may be questioned because olivine probably is in a reaction relation. For the present purposes I assume that the presence of olivine may be ignored. Consequently, I seek experimental conditions which yield hornblende and pyroxene on the liquidus of andesite. The compilation of Stern *et al.* (1975) suggests that compositionally similar andesitic liquids have hornblende and clinopyroxene on the liquidus if the temperature is below about 980°C and the liquid contains more than about 10 weight percent H_2O. The results of Allen and Boettcher (1978) on andesitic bulk compositions are consistent with the above estimate: more than 10 weight percent H_2O in the liquid.

For the second comparison only one assumption is necessary: the hornblende is a hydroxy-hornblende (justified above). I now seek experimental conditions which yield hornblende, pyroxene, and andesitic liquid in a reaction relation with olivine. Holloway and Burnham (1972) and Helz (1973, 1976) encountered andesitic residual liquidus associated with hornblende, pyroxene, and olivine (and in some cases magnetite) at temperatures between about 1000 and 1050°C and with about 6 to 10 weight percent H_2O in the silicate liquid (Table 1, columns 5–8). Allen and Boettcher (1978) found a comparable residual liquid (Table 1, column 9, but no olivine). However, the compositions of residual liquids are difficult to establish for experimental products. The detailed assessment by Helz (1976) suggests that the residual liquids at temperatures greater than about 1015°C (at $P_{H_2O} = 5$ kbar) are less siliceous than the natural liquid. The results of Allen and Boettcher (1978) reveal that the maximum temperature of hornblende stability increases from about 990° to 1050°C as the mole fraction of H_2O in the gas decreases from 1 to about 0.25, consistent with the findings of Holloway (1973). At the mole fraction of 0.25 and a total pressure of 10 kbar, the partial pressure of H_2O would be about 2.5 kbar and there would be about 6 weight percent H_2O dissolved in the liquid. The Hawaiian basalt investigated by Holloway and Burnham (1972), Helz (1973, 1976) and Allen and Boettcher (1978) probably is neither appropriate nor optimal for the generation of natural andesitic residual liquids because of its low concentrations of Al_2O_3 and alkalis. Consequently, it is likely that high-alumina basalt would yield andesitic residual liquids associated with hornblende, pyroxene, and olivine at pressures less than 5 kbar and with P_{H_2O} less than P_{total} at temperatures greater than that found for Hawaiian tholeiite at 5 kbar = $P_{H_2O} = P_{total}$ (namely, greater than about 1015°C).

The above comparisons suggest that andesitic liquids and hornblende are stable to higher temperatures and lesser concentrations of H_2O in basaltic bulk compositions than in andesitic bulk compositions. Probably the availability of olivine (or augite) as a reactant is a principal cause of the greater stability of hornblende in basaltic systems. Other compositional differences [greater Al_2O_3 (Bowen, 1928, p. 111), and alkalis (Cawthorn and O'Hara, 1976)] may help stabilize hornblende, but they cannot be evaluated quantitatively with published information. In sum, comparison of the natural andesitic liquid and associated minerals with experimental products suggests that the natural liquid contained less than 6 weight percent H_2O and quenched from a temperature greater than 1015°C.

Sekine *et al.* [1979] studied experimentally the Asama 1783 andesite. They found no hornblende on or near the liquidus, but did estimate that the residual dacitic liquid (69–72 weight percent SiO_2) of this andesite contained 3.3 weight percent of H_2O at 960°C before extrusion.

Could the concentration and fugacity of H_2O in the included andesitic liquid exceed that of the surrounding residual dacitic liquid? Roedder's (1965) work reveals that olivines are strong enough at 1200°C to contain excess pressures of a few thousand atmospheres in an inclusion. However, a significant gradient of H_2O fugacity from inclusion to rim of crystal would probably disappear by diffusion in a few days or weeks at temperatures near 1000°C, judging from data on Fe, Mg, and O diffusivity in olivine (Buening and Buseck, 1973; Muehlenbachs and Kushiro, 1975). The diffusion of H_2O probably is comparable to that of oxygen because of the similarity in size. The concentration of H_2O (or OH^-) in olivine probably is low in comparison to oxygen; consequently, the concentration gradient and diffusion of H_2O in olivine may be small. Laboratory heating experiments on natural olivines with inclusions of glass suggest that diffusive transfer of H_2O is effective over tens of microns in a few hours at temperatures above 1000°C (Anderson, 1974). Probably both temperature and the fugacity of H_2O in the trapped andesitic liquid associated with hornblende are similar to those in the surrounding melt. Consequently, the most probable conditions for growth of the hornblende from the trapped andesitic liquid are 1080° (Fe–Ti oxides) to 960°C and 100 atm (plausible pressure of froth in vent) to about 1000 atm of H_2O pressure (Sekine *et al.*, 1979).

In sum, the eruptive history, texture, and compositional relations of the hornblende-bearing inclusion suggest that its glass represents an andesitic liquid quenched from a temperature of 1020±60°C and a partial pressure of H_2O between about 100 and 1000 atm. The liquid was in equilibrium with hornblende, probably orthopyroxene, and olivine. The andesitic liquid probably contained a few percent H_2O.

Hornblende associated with natural calc-alkaline basaltic liquid

Observational data

Hornblendes associated with calc-alkaline basaltic material are known from La Soufrière, St. Vincent (Lewis, 1973a,b), Fuego (Rose *et al.*, 1978), and Medicine Lake Volcano, California (Mertzman, 1978). Analyses of these hornblendes and related materials are compared in Table 2. The compositions of the hornblendes are similar and have 13.6 to 16.5 weight percent Al_2O_3, 2.3 to 2.6 weight percent Na_2O, and 1.8 to 2.7 weight percent TiO_2 on an anhydrous basis.

Interpretation

It is uncertain whether any of these hornblendes are in a state of quenched equilibrium with basaltic liquids, because the textural relationships are not definitive and because quenched basaltic matrix is termed andesite by some workers. A case-by-case analysis and interpretation is necessary.

Fuego volcano, Guatemala

The analyzed hornblende (Table 2, column 1) is in the anorthitic core (An92) of a plagioclase phenocryst (An92 to An80). The most closely associated analyzed glass (column 2, Table 2) is an inclusion in the rim of the same crystal. The glass and the hornblende are not in contact. The crystal is depicted in Figure 16 of Rose *et al.* (1978). The glass in the plagioclase is transitional in composition between basalt and andesite.

Rose *et al.* suggested that the hornblende included in the anorthitic core actually grew from a liquid with a more basaltic composition than the inclusion of glass found within the rim of the plagioclase. Their reasoning was as follows: many cores of anorthite from the same eruption contain inclusions of olivine. Subhedral crystals of anorthite (An92–90) are common in olivine phenocrysts. The anorthitic cores of the plagioclase phenocrysts have round corners, comprise a low proprotion of the total plagioclase, are subequant and little zoned. Most of the Fuego plagioclase is oscillatory zoned. The textures of the anorthite cores suggest that it is an early mineral to form in the Fuego magma. Some olivine phenocrysts contain inclusions of basaltic glass (51 percent SiO_2) which are close to the weighted average composition of the bulk rock extruded in the October eruption. The basaltic inclusions and bulk rock probably are similar in composition to the parental liquid from which the earliest crystals formed. The anorthitic cores and the included hornblende probably formed from a liquid with a composition near that of the basaltic glasses (Table 2, column 3).

The temperature of the parental basaltic liquid was about 1030°C; it contained about 4 weight percent H_2O (Rose *et al.*, 1978). Subsequently, Harris (1979) has directly measured 1.6 to 3.2 weight percent of H_2O in inclusions of glass in olivine phenocrysts from Fuego. The lower concentration of 1.6 weight percent H_2O applies to parental liquid in Fo77 olivine. Accordingly, a revised estimate of $1030 \pm 50°C$ and 1.6 weight percent H_2O is preferable for the Fuego liquid which probably precipitated the hornblende.

La Soufrière, St. Vincent

Lewis's (1973a,b) descriptions show that vesicular and microcrystalline dark interstitial material touches hornblende as well as olivine, plagioclase, pyroxene, and magnetite in xenolith 770. The interstitial material (termed scoria by Lewis) analyzed by him is basaltic in composition (column 5, Table 2). Lewis (written communication, 1979) considers his separate to be a good one, little affected by products of weathering and contaminating pieces of the crystals from the gabbro. His analyses show that interstitial scoria from different blocks differ in composition, consistent with an indigenous origin of the interstitial material. The most siliceous interstitial scoria comes from a block of gabbro lacking hornblende but containing olivine, plagioclase, pyroxene, and magnetite. I would expect progressive solidification to increase the number of minerals, stabilize hornblende, and enrich the residual liquid in K_2O and SiO_2. Possibly the gabbro with the most siliceous interstitial material originates from a lesser depth. Lewis's data suggest the crystallization of hornblende from basaltic liquid.

Little Mt. Hoffman, California

Olivine phenocrysts in a basaltic lava from a vent of Modoc Basalt (Powers, 1932) contain subround to irregular inclusions of hornblende (Mertzman, 1978). Olivine phenocrysts in the scoria of the cinder cone (Little Mt. Hoffman) at the source of the flow have round inclusions of devitrified glass, but no hornblende (A. T. Anderson, unpublished data). The compositions of the hornblende and the groundmass of the basalt are given in Table 2, columns 6 and 7.

Because the hornblende occurs included in olivine phenocrysts in basaltic lava, Mertzman (1978) reasonably argued that the hornblende formed from basaltic liquid. The occurrence of hornblende included in olivine together with andesitic glass (see Asama, above) suggests possible alternative interpretations: (1) the olivines with hornblende are xenocrysts derived from an andesitic environment, (2) the hornblendes are daughter crystals which crystallized after the trapped melt attained an andesitic composition by crystallizing olivine. Mertzman's figures show that the hornblende is associated with microcrystalline material (probably formerly liquid). Because of its round shape and association with microcrystalline material, it is likely that the hornblende grew from trapped liquid after it had crystallized olivine. Growth of hornblende from supercooled liquid at a pressure less than 1000 atmospheres is a third possibility. The composition of the liquid from which the hornblende in the Little Mt. Hoffman basalt formed is uncertain. Mertzman (written communication, 1979) notes that the 0.1 weight percent of K_2O in the Little Mt. Hoffman hornblendes suggests that the liquid from which they formed had less than about 0.5 percent K_2O. Possibly the groundmass of the Little Mt. Hoffman basalt is enriched in K_2O by contamination (compare studies of East Sand Butte and cinder cone M39 of Anderson, 1976). Additional work on the Little Mt. Hoffman materials is needed to evaluate the alternatives. I suggest that the liquid from which the hornblende grew was richer in SiO_2 than is the bulk rock because of crystallization of olivine. Probably the liquid was similar in composition to that of the calculated groundmass given as column 7 of Table 2. The composition is that of a basaltic andesite.

Mertzman (1978) extrapolated the results of Yoder and Tilley (1962) on the Warner high-alumina basalt to estimate that the hornblende initially formed at pressures greater than about 12 kbar. In my judgement Mertzman's application and extrapolation of Yoder and Tilley's work is not justified, because the hornblende in question probably grew from a more siliceous liquid with a greater Fe/(Fe + Mg) ratio than the Warner basalt.

Summary

Evidence for the crystallization of hornblende from natural calc-alkaline liquids at least as basic as basaltic andesite (about 54 weight percent SiO_2) is compelling. The data of Rose *et al.* (1978) and Lewis (1973a,b) on ejecta of Fuego and Soufrière volcanoes, respectively, suggest that hornblende grows stably from some high-alumina basalt liquids with about 51 weight percent SiO_2 at temperatures near 1030°C. The basaltic melts are comparatively rich in Fe and poor in Mg and crystallize anorthitic plagioclase (commonly greater than An85), olivine (Fo84 to 66), and magnetite, as well as hornblende.

Experimental results (Helz, 1973, 1976) demonstrate the crystallization of hornblende at crustal pressures from basaltic andesite but not from basaltic liquids. As argued above for andesitic liquids, the crystallization of hornblende is fostered by greater concentrations of alumina and alkalis and $P_{\text{total}} > P_{H_2O}$ probable for natural high-alumina basaltic liquids compared to the Hawaiian basalt studied by Helz. The Warner high-alumina basalt studied by Yoder and Tilley (1962) has atypically greater MgO, MgO/(MgO + FeO), and low alkalis for basaltic members of calc-alkaline magma series. Rose *et al.* (1978) argued that the smaller MgO/MgO + FeO) ratio for Fuego high-alumina basalt would have the effect of making its olivine liquidus temperature about 80°C less than that of the Warner basalt. The difference might permit liquidus hornblende for basalt with a concentration of about 5 percent H_2O in the liquid if $P_{H_2O} = P_{\text{total}}$. Experimental results are not consistent with crystallization of hornblende from some natural high-alumina basaltic liquids with less than a few weight percent H_2O.

General discussion

The facts and interpretations outlined above suggest that hornblende crystallizes from andesitic and basaltic liquids at crustal pressures. Most such hornblende probably is a product of a reaction between liquid and olivine, as first suggested by Bowen (1928, p. 61). The field and textural evidence of plutonic rocks is consistent with crustal formation of hornblende by reaction between liquid and olivine (Miller, 1938; Best and Mercy, 1967; Lewis, 1973b, Ikeda, 1976; Walawender, 1976; Mullan and Bussell, 1977). The 10^4- to 10^6-year lifetimes of subduction-zone volcanoes (McBirney *et al.*, 1974; Rose *et al.*, 1977; Mertzman, 1977; McBirney, 1978), the shorter-term variations in compositions of extruded products (Crandell and Mullineaux, 1973; Crandell *et al.*, 1962; Newhall, 1979), and the 1 km^3 and smaller volumes of products of most individual eruptions, as well as the larger volumes of rare caldera-forming eruptions (Smith, 1979), suggest that the roots of subduction zone volcanoes have thicknesses less than about 1 km and solidify (and differentiate) on time scales appropriate for cold (crustal) environments. Geophysical models of Cenozoic island arcs suggest they consist mostly of rock denser than andesite (for example, see Grow, 1973). Gabbroic rocks, including hornblende gabbro, have appropriate densities consistent with Kuno's (1968) model of a gabbroic crust in island arcs. Dominant hornblende gabbro in island arcs is particularly appealing because it can yield derivative magmas with the calcium-rich cores of plagioclase crystals, the isotopic ratios of strontium and lead, and the bulk compositions typical of many rocks in granodioritic batholiths (Piwinskii and Wyllie, 1968; Faure and Powell, 1972; Doe, 1967; Wyllie, 1977). The basaltic and andesitic liquids from which hornblende forms appear to contain 1.6±0.3 (Harris, 1979) to 4±2 weight percent of H_2O (Rose *et al.*, 1978; Anderson, 1979). The temperature at which hornblende forms in such liquids is probably between 1080° and 960°C (see above).

Various factors probably contribute to the crystallization of hornblende from natural basaltic and andesitic liquids with smaller concentrations of H_2O than the minimum of about 6 weight percent suggested by experiments (Yoder and Tilley, 1962; Holloway and Burnham, 1972; Green, 1972; Helz, 1973, 1976; Stern *et al.*, 1975; Allen and Boettcher, 1978): (1) olivine commonly is present as a reactant in natural associations; (2) natural liquids have some CO_2 in addition to H_2O (Harris, 1979), consequently $P_{H_2O} < P_{total}$; (3) natural basaltic liquids associated with calc-alkaline magma series have greater concentrations of alumina and alkalis than Hawaiian basalts used in experiments; (4) natural calc-alkaline basaltic liquids have smaller MgO/(MgO + FeO) and greater concentrations of alkalis than the Warner basalt used in experiments. All these differences probably enlarge the field of stability of hornblende beyond that found in experiments. Reaction with olivine and other factors probably foster the crystallization of hornblende in some natural basaltic and andesitic liquids with less than 6 weight percent of H_2O, as suggested by the natural occurrences described above.

Reaction between olivine and liquid yielding hornblende acts to minimize the increase in Fe/(Mg + Fe) ratio in derivative liquids. Two factors are significant in minimizing the increase in Fe/(Mg + Fe): (1) reaction between liquid and olivine; (2) crystallization of a hornblende-bearing assemblage of minerals in place of an equivalent anhydrous assemblage.

The effect of reaction was emphasized by Bowen (1928, p. 61). With reaction magnesium-rich olivine tends to buffer the Fe/(Mg + Fe) ratio of crystallizing minerals and residual liquid. Helz (1976) noted that the Fe/(Mg + Fe) ratio of pyroxenes and residual liquids *decreases* with crystallization in part of the range of solidification of hornblende, for example. Reaction with magnesium-rich minerals is an effective mechanism which minimizes increases in the Fe/(Mg + Fe) ratio of residual liquids.

The influence on Fe/(Mg + Fe) of the crystallization of a hornblende-bearing assemblage in place of an equivalent anhydrous assemblage of minerals is complex and disputed (see Ringwood, 1974 and Allen and Boettcher, 1978 for contrasting views). What is meant by "equivalent"? Consider the hornblende-out surface of Figure 1. The mineralogy above the surface and the composition of the liquid on the surface vary with P, T and X_{H_2O}. Many definitions of "equivalent" are possible. I adopt the following definition because it seems consistent with most petrological discussions regarding the role of hornblende in the formation of calc-alkaline rock series: on any surface marking identical bulk compositions of liquids, regions with different solids are equivalent.

For a given increment of crystallization how do the Fe/(Mg + Fe) ratios of residual liquids in two equivalent fields compare? For a given bulk composition (H_2O-free), the liquidus surface is one (and possibly the only) surface with identical compositions of liquids. Consider the difference between the Ol + Pl and the Ol + Hb fields. I assume that the equilibrium composition of olivine on the liquidus is everywhere the same (Roeder and Emslie, 1970). In general the Fe/(Mg + Fe) of hornblende is greater than for associated olivine (Helz, 1973; Lewis, 1973a,b). However, the effect on Fe/(Mg + Fe) of the residual liquid depends on the proportions of the crystallizing minerals as well as on their compositions. The net iron enrichment caused by crystallization of Ol + Hb possibly is greater than that for Ol + Pl. Probably the variation of Fe/(Mg + Fe) of residual liquids with equilibrium crystallization of equivalent hornblende-free and hornblende-bearing assemblages is complex, but not as large as the variations caused by fractional (as opposed to equilibrium) crystallization. I agree, therefore, with Cawthorn and O'Hara (1976) that the omission of iron from their experiments probably is not crucial to an evaluation of the role of hornblende. My emphasis is on reaction, however, rather than fractionation.

Minor increase in Fe/(Mg + Fe) is a characteristic feature of calc-alkaline magma series (Fenner, 1926; Kuno, 1950; Miyashiro, 1974). Consequently, the spectrum of rock series found in subduction zone environments (Peacock, 1931; Kuno, 1950, 1959) can be related in part to variable reaction between olivine and liquid yielding hornblende: in general the more hornblende, the more calcic and the less iron-enriched (less tholeiitic) the series. Many tholeiitic series are calcic, however (for example Higashiyama, Isshiki, 1963) and have basaltic members with small concentrations of alkalis. The concentration of alkalis in the parental liquid is important. Series lacking hornblende probably are tholeiitic or alkalic and tend to have groundmass pigeonite. Variable production of hornblende by reaction between liquid and olivine can help explain variable iron-enrichment and lime-alkali index of many subduction zone magma series.

Implications

The probable crystallization of hornblende within the crust from subduction zone basaltic liquids with less than 6 weight percent H_2O has implications for: (1) the genesis of andesite, (2) the temperature above the Benioff zone, (3) dehydration of subducted oceanic crust, and (4) the origin of continental crust.

Genesis of andesite within the crust is implied by the crustal formation of hornblende gabbro. As discussed above, the Fe/(Mg + Fe) ratio and calc-alkalic index for subduction zone magma series are explicable according to crystallization of hornblende by reaction between olivine and liquid. Although the storage and release of H_2O in and from hornblende in subducted oceanic crust may be important in initiating subduction-zone magmatism, reactions between hornblende and liquids in the Benioff zone probably have no direct influence on the characteristics of magma series in subduction zones (compare Green and Ringwood, 1968; Green, 1972; Boettcher, 1973, with Stern *et al.*, 1975; Cawthorn and O'Hara, 1976; Allen and Boettcher, 1978).

Temperatures greater than about 1000°C are implied by basaltic liquids with less than about 6 weight percent H_2O. If subduction zone basaltic liquids originate between the Benioff zone and the surface, then the temperature must be at least as high as 1000°C somewhere in the interval. Geophysical models of subduction zone processes generally yield lesser temperatures, particularly close to the relatively cold Benioff zone (compare Andrews and Sleep, 1974; Anderson *et al.*, 1976, with Hasebe *et al.*, 1970; Ito, 1978). In order to be consistent with volcanological and geological data, geophysical models should yield temperatures in excess of 1000°C in the magma path between the Benioff zone and the volcanic front, as has been emphasized by Hasebe *et al.* (1970).

Some of the H_2O subducted as oceanic crust is probably not returned to the surface by the outgassing of parental basaltic liquids in subduction zones. There is an average of about 1 to 2 weight percent of mineralogically-bound H_2O in the combined oceanic crustal layers 2 (Melson *et al.*, 1968; Humphris and Thompson, 1978) and 3 (Melson and Thompson, 1971; Prinz *et al.*, 1976; Ito, 1979; Anderson *et al.*, 1979). Parental basaltic liquids of subduction zones probably contain an average of about 2 to 4 weight percent H_2O (Eggler, 1972; Anderson, 1973, 1979; but see also Marsh, 1976; Garcia *et al.*, 1979; and Sekine *et al.*, 1979, who estimate lower concentrations of H_2O). The ratio of mass production of crust in subduction zones (continental growth) to that at oceanic ridges is about 0.2 (Anderson, 1974), based on the ratios of cross-sectional areas of Cenozoic oceanic island arcs (Murauchi *et al.*, 1968; Grow, 1973) and the estimated cross-sectional areas of subducted oceanic crust implied by late Cenozoic local rates of plate convergence (Chase, 1972). If all the H_2O bound in subducted oceanic crust returns to the surface by first entering into basaltic parental liquids, the expected concentration of H_2O in the liquids ranges from 5 (1/0.2) to 10 (2/0.2) weight percent. The estimates of H_2O actually present (2 to 4 percent) are uncertain, but are consistent with the notion (Anderson *et al.*, 1979) that H_2O is released from dehydrating chlorite (the principal mineralogical residence of H_2O in oceanic crust) at too shallow a depth (Delany and Helgeson, 1978, but see Jenkins, 1979) to contribute to melting in subduction zones. The H_2O associated with the parental liquids of subduction zone magmas is similar in amount to the H_2O supplied by amphiboles in the oceanic crust (Ito, 1979).

A complex origin of continental crust is implied by parental basaltic liquid and hornblende gabbro in subduction zones. A principal idea regarding the formation of continental crust involves the postulated production and accretion of andesitic island arcs (Wilson, 1954, p. 206), because average continental crust is andesitic in composition (Goldschmidt, 1933; Taylor, 1967). The chemical composition of the bulk and lower continental crust is uncertain and debated (see Taylor and McLennan, 1979, and Tarney and Windley, 1979 for contrasting views). If the bulk of Cenozoic island arcs is composed of hornblende gabbro, then how can the andesitic composition of average continental crust be explained? The implication of dominant hornblende gabbro in island arcs is that continental crust either was made differently before Cenozoic times or is further differentiated by additional processes.

Note added in proof

The following important article appeared after this paper was accepted for publication: Ritchey, J. L. (1980) Divergent magmas at Crater Lake, Oregon: products of fractional crystallization and vertical zoning in a shallow, water-undersaturated chamber. *J. Volcanol. Geothermal Res., 7,* 373–386.

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