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ASSIMILATION OF ULTRAMAFIC ROCK IN SUBDUCTION-RELATED MAGMATIC ARCS[1]

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ABSTRACT

Assimilation of ultramafic rock by fractionating magma may be an important process in the genesis of subduction-related magmatic arcs. Physical conditions, characterized by low viscosity, fractionating mafic magma, and high wall rock temperatures, are favorable for interaction between magma and rock in the upper mantle. Kinetic and equilibrium constraints determine the availability of wall rock for reaction and the ratio of mass assimilated vs. mass crystallized (*Ma*/*Mc*). The exact value of *Ma*/*Mc* is difficult to predict but, in general, should vary from near 1.0 to about 0.4 for mafic magma reacting with peridotite at high temperature. For any positive value of *Ma*/*Mc*, the effect of assimilation of magnesian rock in fractionating magma is to produce a less iron-enriched, more alkaline derivative liquid than would be produced by crystal fractionation alone. A method is presented for evaluating the effect of combined assimilation and crystal fractionation (*AFC*) which permits continuously changing values for the crystal/liquid distribution coefficient, *Ma*/*Mc*, and the composition of the assimilate, unlike modified versions of the integrated Rayleigh equations in which these parameters must be constant over the entire crystallization interval. A comparison of the concentration of compatible vs. incompatible elements shows that, in principle, even in the absence of isotopic or trace element discriminants, magma series produced by *AFC* may be distinguished from those derived by crystal fractionation alone. In *AFC*, the concentration of a compatible element in many cases approaches a steady state value, while the concentration of an incompatible element increases exponentially.

INTRODUCTION

Although studies of assimilation of felsic material in mafic silicate liquids have become increasingly popular and fruitful in the past few years, (e.g., Grove et al. 1982; DePaolo 1981*a*; Watson 1982*a*; Watson and Jurewicz 1984), little attention has been paid to the assimilation of mafic and ultramafic rocks. However, such a process could be important in the evolution of some rock series. Whereas assimilation of crustal material is limited by the thermal requirements of heating wall rock to magmatic temperatures, assimilation of ultramafic rock by fractionating magma in the upper mantle is subject to no such constraint. Nevertheless, there is an instinctive resistance to considering the effect of assimilation of refractory rock in more "felsic" liquids at temperatures below the solidus for the rock. As shown by Bowen (1922*a*), there is no theoretical basis for this reluctance.

Solid phases out of equilibrium with a liquid will react with the liquid. Bowen observed that the heats of mixing in silicate liquid systems were negligible in comparison with the heats of fusion of most silicate minerals. The enthalpy change during assimilation reactions at constant temperature can be approximated by the difference between the heat of fusion of the assimilate and the heat of crystallization of phases with which the magma is saturated. If the solid to be dissolved is below its melting temperature, and if the magma is saturated in less refractory members of the same reaction series (Bowen 1922*b*), then dissolution results in crystallization of an energetically equivalent mass of saturated phases, the mass crystallized generally being larger than the mass dissolved. These considerations are not path dependent. It is equally valid to view such reactions as addition of liquid components to a refractory solid phase, decreasing the mass of liquid and increasing that of the solid. As long as the mass assimilated is small relative to the mass crystallized, reactions between mantle peridotite and basaltic magma involve a decrease in the entropy and volume of the solid-liquid system; i.e., reactions will often be exothermic at constant temperature. (Note that this reasoning does *not* apply to assimilation of phases across a cotectic "valley" in

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the liquidus surface or to assimilation of less refractory phases in a reaction series. In general, $\Delta H = Ma \cdot \Delta H_f^a - Mc \cdot \Delta H_f^c$, where ΔH is the reaction enthalpy, Ma is the mass assimilated, Mc the mass crystallized, and ΔH_f^a and ΔH_f^c are the apparent enthalpies of fusion, per gram, for the assimilate and precipitate at the temperature of reaction. Assimilation reactions are exothermic when $Ma/Mc \cdot \Delta H_f^a/\Delta H_f^c < 1$, and endothermic when this term is greater than one.)

Formation of pyroxenite by reaction between mantle peridotite and more felsic magma has been proposed on a plate tectonic scale by Ringwood (1974), experimentally demonstrated on a microscopic scale by Sekine and Wyllie (1982, 1983), and invoked to explain map and outcrop scale contact relations by Ramp (1975), Kelemen and Sonnenfeld (1983), Evans (1985), and Kelemen and Ghiorso (1986). Irving (1980) and Menzies et al. (1985) presented evidence for cryptic and modal metasomatism of spinel lherzolite wall rock by magma in the mantle. Arculus et al. (1983) proposed that assimilation of ultramafic material in the crust played an important role in the development of an unusual magma series in Papua New Guinea. Additional evidence for reaction between magma and more mafic rocks beneath volcanic arcs, preserved in composite or "hybrid" xenoliths, has recently been presented by Conrad et al. (1983) and Conrad and Kay (1984). They wrote (1984, p. 94) that "textural features in composite xenoliths give evidence for assimilation of wall rock or magma ('primary assemblage') by another magma ('secondary assemblage'), all of which occurs prior to incorporation of the xenolith in the host lava . . . Assimilated phases in the primary assemblage are . . . Mg-, Cr-, and Ni-rich, and are presumably the first fractionates of mantle derived melts."

HYBRIDIZATION OF THE MANTLE IN MAGMATIC ARCS

Magmas formed in the mantle must react with their host rocks, if only in equilibrium exchange reactions with their own refractory residuum. In an idealized, single-stage melting model, partial melts would leave their hosts and pass upward into unmelted mantle. At nearly constant temperature (and pressure), reactions between melt and wall rock would affect the composition of the liquid. Variants of this simple hypothesis have been proposed by Harris (1957), Green and Ringwood (1967), Quick (1981), and Watson (1982*b*) to account for the genesis of alkalic basalt. As these authors have pointed out, such a process would lead to enrichment in the melt of incompatible trace elements, alkalies, and volatiles, while preserving otherwise very "primitive" major element chemistry. In addition, the increasing volatile content of the liquid could cause significant changes in the minimum melting composition of the local mantle-magma system. Furthermore, previous investigators have assumed that magmatic temperature remains constant from initial melting to eruption. Where magma and wall rock temperatures are below the equilibrium temperature of primary melts in the mantle (perhaps 1200 or 1300°C), the result of solid-liquid reaction must be somewhat different. The effect of a combination of assimilation and crystal fractionation on the composition of liquid ascending through cooler upper mantle has not been sufficiently explored.

Mantle tectonite xenoliths are rarely found in volcanic arcs, although study of the conditions of formation of some "cumulate" xenoliths indicate that they originate at upper mantle temperatures and pressures (Powell 1978; Arculus and Wills 1980; Conrad and Kay 1984). Unequivocal exceptions are Itinome-gata, Japan, Kanaga Island, Alaska, and Grenada, Lesser Antilles, where tectonite spinel lherzolite inclusions have been found (Kuno 1967; DeLong et al. 1975; Takahashi 1980; Pope et al. 1981; Arculus pers. comm. 1986). Thermal regimes inferred for subduction-related volcanic arcs (Anderson et al. 1976, 1978, 1980; Blackwell et al. 1982; Tatsumi et al. 1983) have temperatures near 1000°C in the upper mantle. These conditions would lead to crystal fractionation combined with infiltration and assimilation of wall rock by mafic magma derived from lower in the mantle "wedge."

There is little doubt that primary magmas in volcanic arcs are derived from, or at least pass through, the mantle. The scarcity of tectonite lherzolite and harzburgite xenoliths has generally been ascribed to the slow rate of ascent of arc magma as compared to continental, alkalic basalts which rise rapidly from the mantle and are typically richer in such inclusions. Another, related possibility is that much of the upper mantle in mature volcanic arcs has been so thoroughly altered by slow moving melts that it does not preserve the characteristic texture and mineralogy of oceanic upper mantle. Xenoliths derived from such altered mantle will be petrographically similar to magmatic cumulates.

Gill (1981) summarized data on the seismic refraction profiles of volcanic arcs. "Typical" oceanic crust is about 8 km thick, whereas island arc crust extends to at least 15 km and as much as 30 km depth in some arcs. The thickening of island arc crust has been ascribed to accumulation of a volcano-sedimentary pile at the surface, coupled with "underplating" of gabbroic cumulates in magma chambers at depth (e.g., Kuno 1968; Conrad and Kay 1984). However, the formation of pyroxenite and gabbroic rocks with appropriate seismic velocities might also be due, in part, to reaction between mantle and magma en route to the surface.

If such "hybridization" reactions do occur, they would have an effect on the thermal structure of subduction-related magmatic arcs. Most dehydration and melting reactions result in positive changes in entropy and volume, (except at very high pressure), and thus are endothermic. The absorption of heat by dehydration reactions in the underthrust plate in subduction zones has been considered an important parameter in determining the geothermal gradient at convergent margins (Anderson et al. 1976, 1978). Most of the fluid evolved from the downgoing slab must react with rock above the subduction zone. The high geothermal gradient observed in magmatic arcs may be due to addition of H_2O, silica, and alkalis to the mantle wedge. Heat supplied by exothermic hydration and "silicification" reactions could initially increase the temperature of parts of the mantle-magma system, until temperature is buffered by the heat of fusion near the solidus of the modified mantle.

"RATE" OF ASSIMILATION VS. CRYSTALLIZATION

The limiting factors in assimilation processes include: (1) the ratio of mass assimilated to mass crystallized (Ma/Mc; note that this ratio can be thought of as a mass balance or as the integrated ratio of the rate of assimilation, dMa/dt, divided by the rate of crystallization, dMc/dt) and (2) the ability of a magma to react with a significant fraction of the host rock. These two factors are linked: if rapid crystallization armors the host in new material, no assimilation of the original wall rock will occur. The crystallization rate is largely a function of the rate of temperature change. When temperature is constant, the rate of crystallization may be very slow and equal to the rate of assimilation for a magma in major element equilibrium with its host ($Ma/Mc = 1$). Under conditions of rapidly falling temperature where the wall rock is considerably cooler than the melt, rapid crystallization will be coupled with very slow assimilation. Finally, if Ma/Mc is small and the magma can react with a sufficiently large mass of wall rock, then the process of combined assimilation and crystallization will produce potentially important solid products but will not be expressed in compositional variation in those magma series which reach the surface of the earth.

The ability of a melt to infiltrate its host rock becomes important when the rate of crystallization is slow. Watson (1982*b*) and Stolper (1980) have shown that basaltic magma in equilibrium with its host can infiltrate dunite and harzburgite under conditions of nondeviatoric stress, as predicted theoretically (Bulau and Waff 1979; Waff and Bulau 1979). Viscosity must influence the kinetics of infiltration and is related to the surface energy difference which determines the equilibrium "wetting angle" in a given solid-liquid system (Bulau and Waff 1979; McKenzie 1984).

Another factor which may influence transfer of magmatic components into wall rock is the concentration of H_2O, even in fluid-undersaturated systems. The gradient between the chemical potential of H_2O in a hydrous magma and the chemical potential of H_2O in an anhydrous xenolith (or wall rock) must drive diffusion of H_2O into the xenolith. This may result in development of an intergranular film of H_2O, as originally suggested by Nockolds (1933). At low fugacities of H_2O, an intergranular film is not a macroscopically homogeneous fluid "phase." Nevertheless, Walther and Wood (1984) calculated that, in the presence of intergranular films of H_2O as narrow as 10 Å in width, diffusion of other components would be several orders of magnitude faster than "dry" grain boundary diffusion.

Under conditions of nearly constant temperature, the kinetic constraints outlined above control the mass of mantle wall rock available for reaction with magma but do not influence directly the value of *Ma*/*Mc*, which will largely be determined by equilibrium reaction stoichiometry. Predicting equilibrium *Ma*/*Mc* accurately for natural solid-liquid reactions is problematic. As an example, consider the reaction:

(1) Mg-rich olivine + liquid$_1$
= low-Ca pyroxene + liquid$_2$.

Thermodynamic calculations using a solution model for natural silicate liquids (Ghiorso et al. 1983; Ghiorso 1985; Ghiorso and Carmichael 1985) predict *Ma*/*Mc* of about 0.65 for natural basaltic liquid assimilating olivine (Fo90) and producing orthopyroxene (En77) at constant temperature and pressure (Kelemen and Ghiorso 1986). This *Ma*/*Mc* value is nearly that of the stoichiometric relation

$$\mathrm{Fo} + \mathrm{SiO_{2(liq)}} = 2\ \mathrm{En}$$

However, Bowen (1922) showed that the isothermal reaction at 1550°C, 1 bar, in the binary Mg_2SiO_4-SiO_2 system has stoichiometry close to

$$\mathrm{Fo} + \mathrm{SiO_{2(liq)}} + 5\ \mathrm{MgSiO_{3(liq)}} = 7\ \mathrm{En}$$

with *Ma*/*Mc* = 0.2. Reaction stoichiometry is partly a function of temperature. At the binary peritectic point, *Ma*/*Mc* = 0.06; at the binary eutectic the value is 0.23. There remains, however, a large discrepancy between reaction stoichiometry calculated from binary phase relations and that predicted for a natural system. This discrepancy is due to the influence of liquid components other than MgO and SiO_2 on the solid-liquid system.

Consideration of ternary systems, rather than the Fo-SiO_2 binary, will illustrate this point. Figure 1 illustrates the lever rule method by which Bowen derived isothermal reaction stoichiometry in the binary and a similar geometric method for determining reaction stoichiometry in a ternary system involving forsterite, silica, and a third, unspecified, oxide component. In figure 2, solutions using this method are contoured in a generalized ternary diagram, in which the unspecified third oxide component is denoted MO.

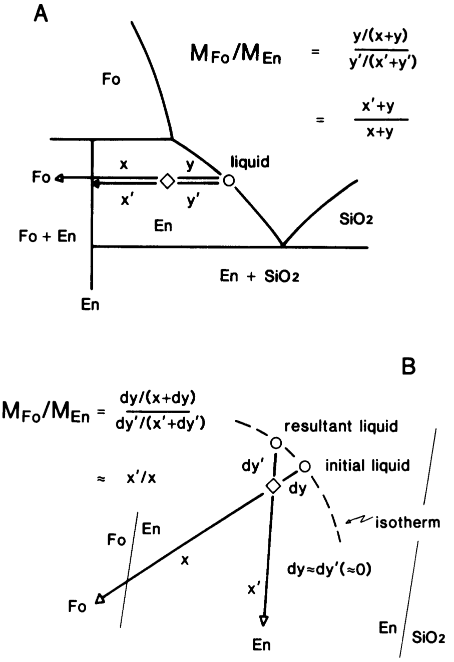

FIG. 1.—Graphical methods for determining stoichiometry of the reaction forsterite + liquid = (clino)enstatite at constant temperature. (Mass forsterite/mass enstatite = *Ma*/*Mc*.) (*A*) In the binary Mg_2SiO_4 − SiO_2 system, the composition of liquid saturated with $MgSiO_3$ is isothermally, isobarically invariant. For *L* = wt % SiO_2/(wt % SiO_2 + wt % Mg_2SiO_4) in the liquid, *Ma*/*Mc* = (*L* − 0.3)/L. (*B*) In ternary systems with components Mg_2SiO_4, SiO_2, and an arbitrary third component, MO, the ratio *Ma*/*Mc* can be determined at constant temperature using the lever rule, provided: (1) both forsterite and the pyroxene formed lie on the high temperature side of the isotherm; (2) the isotherm is not parallel to the vectors x or x′; and (3) there is little or no solid solution moving the composition of pyroxene away from $MgSiO_3$, or the exact composition of the pyroxene formed is known and the length of the vector x′ is adjusted accordingly.

Application of this general diagram in determining isothermal reaction stoichiometry in the ternary forsterite-anorthite-silica system is also shown in figure 2. Note that the pyroxene formed in this system may not lie on the ternary plane and certainly is slightly displaced from $MgSiO_3$ on the Fo-SiO_2 join. However, such a slight displacement has a very minor effect in this application. On the

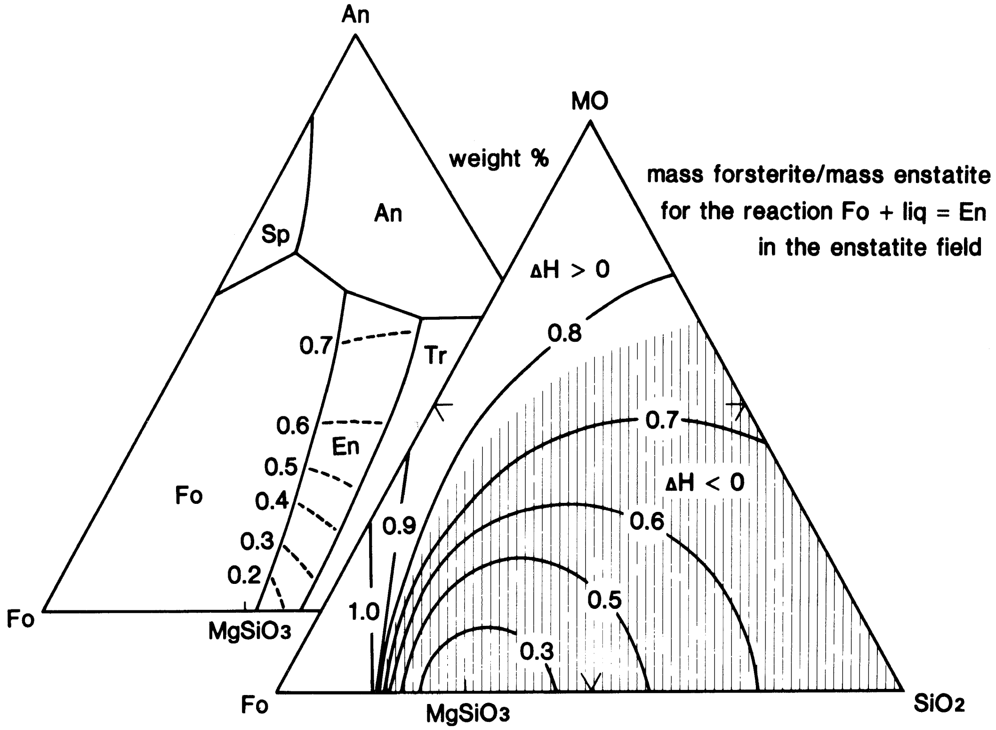

FIG. 2.—A generalized ternary system with components Mg_2SiO_4, SiO_2, and an unspecified third component, denoted MO. The ternary diagram is contoured for values of the ratio of mass forsterite (Fo) consumed to mass enstatite (En) produced (*Ma*/*Mc*) in the reaction Fo + liquid = En. The contours are only valid within the enstatite field in any specific ternary system; as an illustration, the pertinent contours are shown in the enstatite field of the forsterite-silica-anorthite ternary phase diagram determined by Anderson (1915). The ruled pattern in the generalized ternary diagram shows the area in which the reaction is exothermic; i.e., where the apparent heat of crystallization of enstatite exceeds the apparent heat of fusion of forsterite. The term "apparent heat of fusion" refers to enthalpy change for dissolution of a pure solid phase, in a liquid of a different composition, at some temperature below the melting temperature of the pure phase on its own composition. Evaluating this parameter requires knowledge of the solid and liquid heat capacities, heat of fusion, and melting temperature for each mineral composition; such data are available in Ghiorso and Carmichael (1980) and Stebbins et al. (1984). Calculated enthalpy change is less than zero for $Ma/Mc < 0.77$ at 1300°C, $Ma/Mc < 0.75$ at 1000°C. At a given temperature, each value of *Ma*/*Mc* can be replaced with a value of ΔH. For instance, the approximate enthalpy change along the 0.6 contour is about −35 cal/gm En produced at 1300°C, and −27 cal/gm En produced at 1100°C.

pyroxene-anorthite cotectic, the effect of isothermal assimilation of forsterite would be the formation of crystals of which about 80% were pyroxene, and 20% were anorthite. *Ma*/*Mc* would be approximately 0.75, as in the pyroxene field immediately adjacent to the cotectic.

In iron-bearing systems, assimilation of forsterite by liquids in the low-Ca pyroxene field would lead to crystallization of a low-Ca pyroxene which might not lie in the ternary plane and could be substantially displaced from $MgSiO_3$ toward the MO apex. As a consequence, the ratio *Ma*/*Mc* would generally be somewhat smaller than that given on the contoured diagram. Nevertheless, we can see that *Ma*/*Mc* for reaction (1) could plausibly vary from less than 0.1 to 1.0 or more in some simple ternary systems; values of 0.4 to 0.8 are likely for natural systems.

We have considered the reaction Fo + liq = En as an example because of the great body of data available on ternary Fo-SiO_2-MO systems. Other reactions are likely to be at least as important in mantle-magma systems. In fractionating basalts saturated with olivine, for instance, the most important of these is:

$$(2)\quad \text{olivine}_1 + \text{liquid}_1 = \text{olivine}_2 + \text{liquid}_2$$

where olivine produced is richer in iron than olivine consumed, and Ma/Mc is slightly less than 1.

For liquids saturated with high-Ca pyroxene and/or plagioclase, and not with olivine or low-Ca pyroxene, the ratio Ma/Mc at constant temperature may be very large. In the ternary system forsterite-anorthite-diopside (determined by Osborn and Tait 1952), assimilation of forsterite in liquids saturated with diopside or anorthite at constant temperature would first dissolve any reservoir of crystals in the system ($Ma/Mc < 0$). When the solids were exhausted, the liquid would move toward the forsterite apex without consequent crystallization (infinite Ma/Mc), until it saturated with forsterite ($Ma/Mc = 1$). Obviously, this process will be endothermic until the liquid is saturated in forsterite.

When assimilation occurs across a cotectic "valley" in the liquidus surface, constant temperature may not be a reasonable boundary condition, even where wall rock and magma are both at the same initial temperature. Isenthalpic conditions may be a more reasonable end-member constraint for calculating the effects of such reactions in the mantle. Using apparent enthalpies of fusion of fosterite, diopside, anorthite, and albite (derived from data on heats of fusion, temperatures of fusion, and liquid and solid heat capacities from Ghiorso and Carmichael 1980 and Stebbins et al. 1984), we can calculate isenthalpic reaction stoichiometry for the following reactions:

(3) Fo + liq = Di ($Ma/Mc = 0.76$ at 1300°C, 0.80 at 1000°C);

(4) Fo + liq = An ($Ma/Mc = 0.51$ at 1300°C, 0.56 at 1000°C);

(5) Fo + liq = Ab ($Ma/Mc = 0.35$ at 1100°C, 0.36 at 1000°C).

At lower temperatures, discontinuous reactions involving hornblende may become important. In experimental runs in which

(6) Ca-rich pyroxene + liquid = hornblende (+ minor phases),

the mass ratio pyroxene consumed/hornblende produced varied from 0.23 (Holloway and Burnham 1972) to 0.62 (Helz 1982). Both of these results are for the same natural rock composition (1921 Kilauea tholeiite) at 5 kb, but the experiments differ in T, f_{H_2O} and f_{O_2}. Furthermore, they represent reaction over a temperature interval, rather than under isothermal, isobaric conditions.

EFFECT OF ASSIMILATION ON DERIVATIVE LIQUIDS

In general, Bowen (1922*a*) suggested that assimilation, particularly assimilation of mafic rock in more felsic magma, could not produce liquids fundamentally different from those produced by fractional crystallization alone. This postulate, combined with the applicability of experimental techniques to models of closed-system fractionation, influenced a generation of igneous petrologists. If derivative magmas were essentially identical, then assimilation was an interesting, and complex, but secondary effect. Under these circumstances, the problem of determining solid-liquid reaction stoichiometry might seem rather arcane.

However, a hypothetical experiment might suffice to show the importance of such reactions on the composition of modified liquids. Envision a mafic magma with Mg-rich orthopyroxene (Opx) on the liquidus. In case (1), a temperature drop, resulting in crystallization of a small amount of Opx (mass = Mc), produces an iron enrichment trend in the liquid, shown schematically in figure 3. In case (2), at constant temperature, addition of a small amount of magnesian olivine (mass = Ma) to the liquid results in the crystallization of the same mass (Mc) of orthopyroxene as in case (1). It has been shown that the equilibrium value of Ma/Mc may vary greatly in basaltic systems. If Bowen's prediction for the binary Mg_2SiO_4-SiO_2 system could be extrapolated to natural systems, Ma/Mc would be close to 0.2 (case 2*a*). Case (2*b*) illustrates the effect of a larger Ma/Mc, which is believed to be more characteristic of natural basalt-mantle reaction. Either way, the derivative liquid in case (2) will be less iron-rich, and more alkaline, than in case (1). Reactions involving other phases, for instance Mg-rich olivine + liquid = more Fe-rich olivine, will produce qualitatively similar results as long as the assimilate is more magnesian than the phase(s) with which the liquid is saturated.

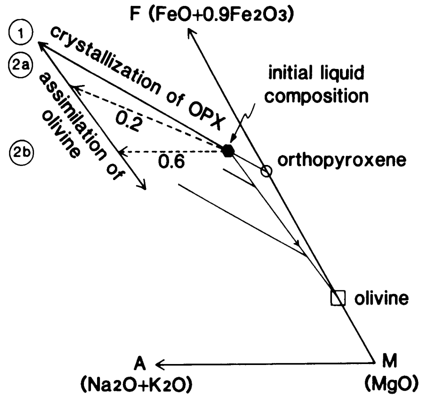

FIG. 3.—Schematic illustration of the effect of assimilation of magnesian olivine in a liquid saturated with more iron-rich orthopyroxene. Vector (1) indicates the compositional change in the liquid due to crystal fractionation, while vectors (2a) and (2b) illustrate changes in liquid composition for various values of mass olivine assimilated vs. mass orthopyroxene crystallized. This diagram would be similar for assimilation of any magnesian phase in liquid saturated with a phase assemblage with lower Mg/(Mg + total Fe). In general, the effect of combined assimilation of ultramafic rock and crystal fractionation is to produce a less iron-enriched, more alkaline derivative liquid than would be produced by crystal fractionation alone.

The general effect of assimilation of magnesian olivine on the liquid line of descent of a fractionating basalt can be seen in figure 4 and table 1, which present results of calculations using a solution model for natural silicate liquids (Ghiorso et al. 1983; Ghiorso 1985; Ghiorso and Carmichael 1985). At a given temperature, the liquid produced by assimilation of magnesian olivine combined with crystal fractionation (*AFC*) has a higher Mg# (100 MgO/(MgO + total Fe as FeO), and higher concentrations of silica and alkalies, than liquid produced by crystal fractionation alone. Relative to the results of crystal fractionation, the solid products produced by *AFC* have a higher mole fraction of forsterite in olivine, a greater proportion of olivine to plagioclase, and a lower mole fraction of anorthite in plagioclase.

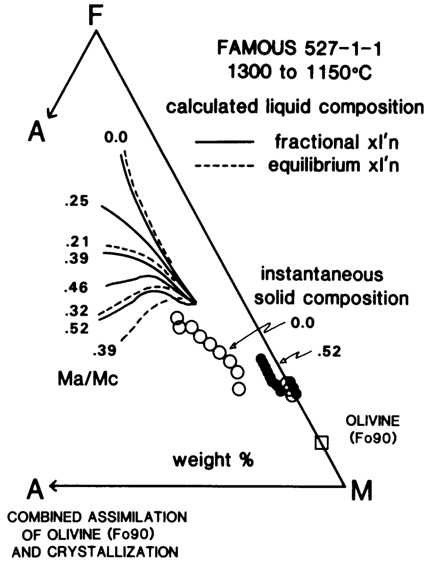

FIG. 4.—*AFM* plot of calculated crystal and liquid compositions for crystallization of a high-Mg MORB, with and without combined assimilation of magnesian olivine (Fo90). The initial liquid composition used was that of FAMOUS 527-1-1, the composition crystallized experimentally by Bender et al. (1978). Calculations were performed using the computer program SILMIN, implementing a regular solution model for silicate liquids (Ghiorso et al. 1983; Ghiorso 1985; Ghiorso and Carmichael 1985). Input parameters for this calculation are initial liquid composition, temperatures (1300 to 1150°C at 10° increments), pressure (3 kb), oxygen fugacity (*FMQ*), composition of the assimilate, and rate of assimilation in grams per °C per 100 gm initial liquid. Resultant phase compositions and phase proportions are calculated, using the computer program to find the minimum free energy state for the system after each increment of temperature and composition change. *Ma*/*Mc* refers to the mass assimilated (input) vs. mass crystallized (calculated) over the interval 1300 to 1220°C. This value is very nearly equal to the calculated "instantaneous" value of *Ma*/*Mc* at 1220°C. For further discussion, please refer to table 1 and to the text.

Assimilation of mafic material in more felsic magma could account for some differences between tholeiitic and calc-alkaline magma series. Intermediate liquids in calc-alkaline suites in many cases have higher incompatible *and* compatible element concentrations than can be produced by fractional crystallization of proposed basaltic precursors (Taylor et al. 1969; Gill 1978, 1981; Stern 1979; Masuda and Aoki 1979; Grove et al. 1982; Arculus pers. comm. 1986). This cannot always be due to assimilation of continental crust. Assimilation of ultramafic rock combined with crystal fractionation should produce just these deviations from a liquid line of descent governed by crystal fractionation alone.

Isotopic indicators have been used to evaluate the presence and degree of assimilation of metasedimentary material in mantle-derived, basaltic magmas (e.g., Grove et al.

TABLE 1

Calculated Phase Compositions and Phase Proportions for Combined Assimilation of Magnesian Olivine (Fo90) and Crystallization of a Primitive MORB (FAMOUS 527-1-1) from 1300 to 1220°C at 3 kb on the FMQ Oxygen Buffer

		Combined assimilation of olivine (Fo90) and fractional crystallization			Combined assimilation of olivine and equilibrium crystallization		
Rate[a]	Initial liquid	0 gm/°C	.4 gm/°C	.6 gm/°C	0 gm/°C	.4 gm/°C	.6 gm/°C
SiO_2	48.65	49.44	50.50	51.11	49.35	51.63	52.81
TiO_2	.74	1.28	1.52	1.67	1.41	2.39	3.04
Al_2O_3	16.45	14.63	15.25	15.54	14.72	15.85	16.38
FeO[b]	8.99	11.96	10.29	9.33	11.97	8.07	5.97
MgO	10.80	8.47	8.03	7.78	8.40	7.16	6.50
CaO	12.11	11.33	11.27	11.25	11.40	11.43	11.47
Na_2O	1.97	2.40	2.72	2.90	2.34	2.98	3.30
K_2O	.09	.11	.13	.14	.12	.16	.19
P_2O_5	.06	.11	.12	.14	.12	.20	.25
Mg#[c]	54.6	41.5	43.8	45.5	41.2	47.0	52.1
		Phase proportions in grams per 100 gm initial liquid.					
Mass liquid		57.06	48.10	43.61	51.83	30.56	24.01
Mass olivine (Fo90) Assimilated		0	32	48	0	32	48
Mass olivine produced		9.98	45.40	63.01	11.17	50.00	67.87
Mole fraction Fo		81.2[d]	81.6[d]	81.8[d]	81.2	82.1	83.0
Mass plagioclase		23.93	27.09	28.79	26.67	35.50	38.48
Mole fraction An		74.6[d]	73.6[d]	73.0[d]	75.0	73.4	72.7
Mass clinopyroxene		8.06	10.42	11.59	9.36	14.92	16.62
Mole fraction Di		84.7[d]	84.4[d]	84.2[d]	84.7	83.9	83.4
Ma/*Mc*[e]		0	.39	.46	0	.32	.39

Note.—For further explanation, please refer to text, and to the caption for figure 4.

[a] Rate of assimilation in grams of olivine (Fo90) added per °C per 100 gm initial liquid.

[b] Total Fe as FeO.

[c] 100 · wt % MgO/(MgO + FeO).

[d] Mole fractions of Fo, An, and Di from the fractional crystallization calculations are for the instantaneous solid composition at 1220°C. All other values are for the total solid composition formed from 1300 to 1220°C.

[e] Cumulative mass assimilated/mass crystallized, evaluated at 1220°C.

1982; DePaolo 1981*a*). This method works well because (a) there is a marked contrast between isotope ratios in mantle-derived basalt and quartzo-feldspathic sediments, and (b) there is often a higher concentration of Nd, Sm, U, Pb, Rb, and Sr in metasedimentary rocks than in basalt. In the case of assimilation of mantle rock by mantle-derived melts, there is virtually no difference in isotope ratios between host and magma, and mantle rocks generally have low abundances of Nd, Sm, U, Pb, Rb, and Sr relative to basalt. In general, isotope systematics cannot be used as geochemical indicators of interaction between melts and mantle in volcanic arcs, although oxygen or magnesium isotopes might be useful in special cases.

DePaolo (1981*b*) has presented a model for the effects of combined wall rock assimilation and fractional crystallization on the composition of an evolving magma. Input parameters are the concentration of an element in the assimilate relative to that in the initial melt (*Ca*/*Cmo*), the bulk crystal-liquid partition coefficient for that element (*D*), and the ratio of mass assimilated to mass crystallized ($r = Ma/Mc$). DePaolo's model treats each of these as a constant throughout the course of fractionation. A more general solution may be obtained using the mass balance

$$Cm' = (Cm \cdot Mm + Ca \cdot Ma - Cc \cdot Mc)/Mm',$$

where *C* refers to concentration, *M* refers to mass, and *m*, *a*, and *c* refer to magma, assimilate, and crystals, respectively. The superscript ′ denotes values of *Cm* and *Mm* after some increment of mass transfer ($Mm - Mm'$). Division by initial concentration, *Cmo*, and substitution, using $r = Ma/Mc$ and $D = Cc/Cm$, yields

$$Cm'/Cmo = (Cm/Cmo \cdot Mm + Ca/Cmo \cdot Ma - D \cdot Cm/Cmo \cdot Ma/r)/Mm'.$$

Results using this algorithm converge for small values of the step ($Mm - Mm'$). Using 1000 intervals from $Mm/Mmo = 1$ to $Mm/Mmo = 0$ produces values of *Cm*/*Cmo* within +/−0.001 of those from DePaolo's equation but also allows modeling with changing *r*, *D*, and *Ca*/*Cmo*.

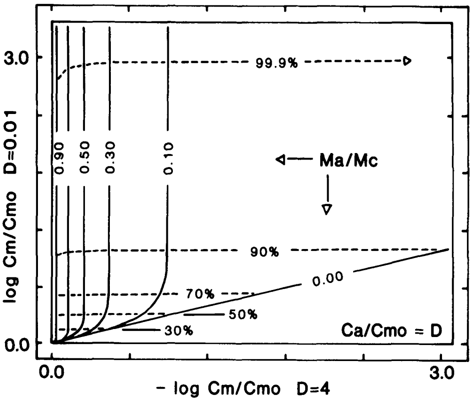

FIG. 5.—"Magma evolution diagram," with (log) abundance of an incompatible element vs. (−log) abundance of a compatible element, illustrating the effect of combined assimilation of mafic material and crystal fractionation on derivative liquids. The concentrations of both compatible and incompatible elements in the magma are expressed as ratios of instantaneous concentration vs. initial concentration (*Cm*/*Cmo*). Values of crystal/liquid partition coefficient (*D*), concentration of elements in the assimilate (referenced to concentration in the initial liquid; *Ca*/*Cmo*), and mass assimilated/mass crystallized (*Ma*/*Mc*), are held constant over the entire crystallization interval for each curve. Assimilate is in chemical equilibrium with initial liquid, i.e., $Ca/Cmo = D$. This boundary condition is chosen to simulate reaction of fractionating basalt with wall rock in the mantle. Values in percent are "percent crystallized": (1 − mass liquid/initial mass liquid) · 100%. The effect of assimilation of mafic material (all curves with $Ma/Mc > 0$) is markedly different from the effect of crystal fractionation alone ($Ma/Mc = 0.0$).

During combined assimilation and fractionation, the abundance of incompatible elements in the liquid increases exponentially while the abundance of compatible elements reaches a steady state. It is desirable to use a method for displaying such relationships which is independent of the fraction of liquid remaining in the system, since this is rarely known for members of a given igneous rock series. One way to do this is simply to compare the (log) abundance of an incompatible element to that of some compatible element on a "magma evolution diagram," as in figure 5. The combined assimilation and fractionation cases form a distinctive signature quite different from that generated by crystal fractionation alone.

In these examples, the value of *D* has been taken as equal to *Ca*/*Cmo*; that is, the magma and the assimilate are taken to be in chemical equilibrium at the beginning of the process, prior to fractional crystallization. Nothing in

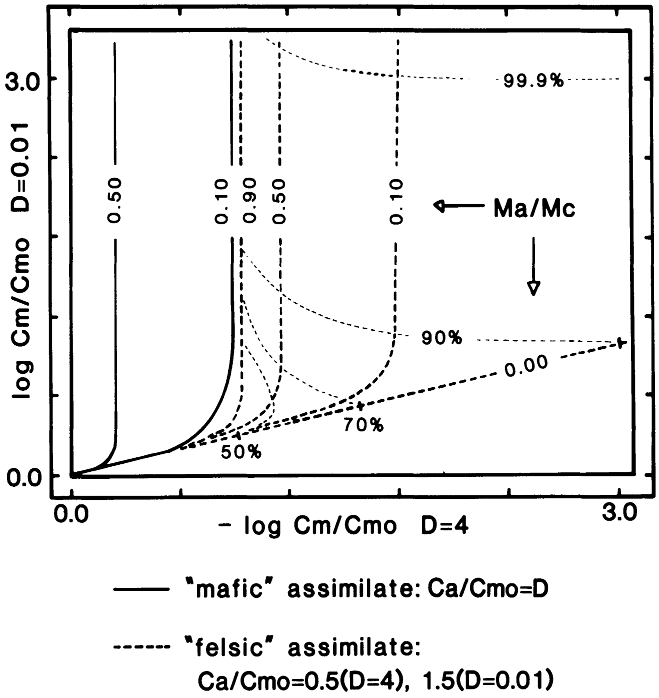

FIG. 6.—Assimilation of mafic material, in chemical equilibrium with initial liquid, compared to assimilation of more felsic material in the same liquid. Explanation of parameters as for figure 5. Assimilation of mafic material produces a more marked effect than assimilation of more felsic material at the same *Ma*/*Mc*.

the model discriminates between a solid and a liquid assimilate (i.e., magma mixing), but the boundary condition that $D = Ca/Cmo$ would not regularly be met in magma mixing processes, nor would the rate of mixing be related to the rate of crystallization, i.e., *Ma*/*Mc* would not be constant or have any predictable variation. Magma mixing can explain a diverse array of chemical variation, but it is not amenable to general modeling.

An illustration of assimilation of a more evolved melt or a more felsic wall rock in a mafic magma is given in figure 6. The two elements being compared have the same crystal/liquid distribution coefficients as in figure 5, but the concentration of the incompatible element is greater in the assimilate than in the initial liquid ($Ca/Cmo = 1.5$), and the concentration of the compatible element is less in the assimilate than in the initial liquid ($Ca/Cmo = 0.5$). The exponential increase in concentration of the incompatible element occurs at lower concentrations of the compatible element. Large values of *Ma*/*Mc* for a felsic assimilate produce the same trend on a magma evolution diagram as small values of *Ma*/*Mc* with a mafic assimilate.

Although this approach could be used to investigate trace element variation in magma series, it is preferable to begin with major element modeling. Mg probably represents a compatible element over the entire course of crystallization of most natural liquids. However, bulk *D*(Mg) would be quite large if olivine alone were crystallizing, around 4 or 5 in mafic liquids, smaller if only pyroxenes were precipitating, and close to 1 if crystallization of plagioclase or oxide phases dilutes the effect of the ferromagnesian minerals. Crystallization of hornblende and biotite, with small, though positive, *D*(Mg), would also reduce the bulk distribution coefficient. Nevertheless, rock series, particularly more evolved members of differentiation sequences, rarely show an increase in Mg with increasing fractionation. *D*(Mg) may vary from 4 (a good value for mafic basalt in equilibrium with lherzolite) to 2. Similarly, K may be incompatible over most of the crystallization range of typical liquids. With decreasing temperature, crystallization of biotite, and/or muscovite could greatly increase the bulk *D*(K) so that it approaches 1. If K-feldspar were stable, this effect would be more marked. *D*(K) may vary from about 0.01 to 1.

Melts at constant temperature in equilib-

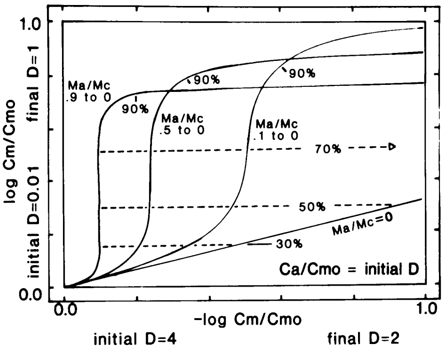

FIG. 7.—Effect of varying crystal/liquid distribution coefficients (*D*) and rate of assimilation vs. crystallization (*Ma*/*Mc*). Explanation of parameters as for figure 5. Parameters are constant to 70% crystallized (1 − mass of liquid/initial mass of liquid = 0.7), then varied linearly to the final value at 100% crystallized. Assimilate is in chemical equilibrium with initial liquid. This diagram is intended to roughly approximate the concentration of K vs. Mg in fractionating magma (initially basalt) with varying rates of assimilation in the upper mantle.

rium with wall rock have a ratio of *Ma*/*Mc* of 1. As long as olivine remains on the liquidus, *Ma*/*Mc* could be between 1 and 0.9 at very slow cooling rates. Reactions between mantle rock and basaltic magma no longer in equilibrium with olivine probably have equilibrium *Ma*/*Mc* of about 0.9 to 0.3 at slow cooling rates. At fast cooling rates, where crystallization due to decreasing temperature is more important than crystallization as a consequence of wall rock reaction, *Ma*/*Mc* will decrease. A magma evolution diagram for varying values of *Ma*/*Mc* and *D* is presented as figure 7.

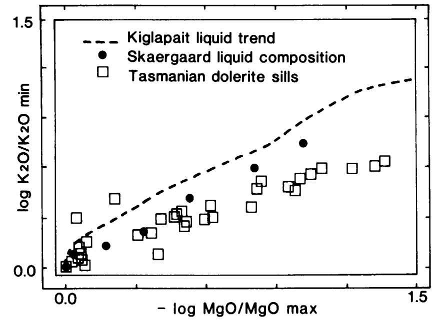

FIG. 8.—Magma evolution plot for mafic intrusive bodies that underwent crystal fractionation (McDougall 1962; Morse 1981; Wager and Brown 1967), with very minor amounts of assimilation of crustal material (DePaolo 1985; Leeman and Dasch 1978), at high levels in the crust.

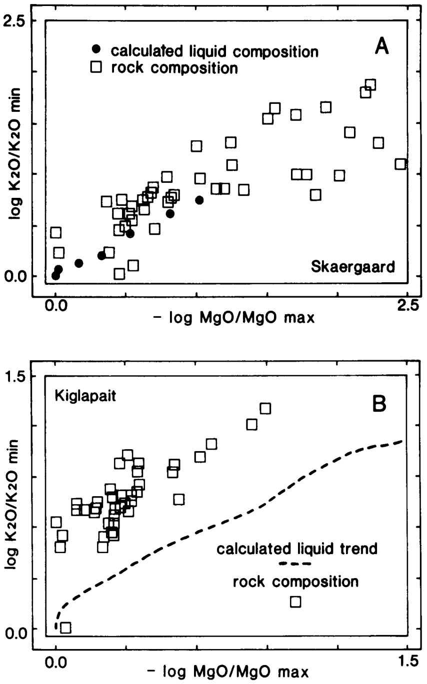

FIG. 9.—Both Skaergaard (*A*) and Kiglapait (*B*) liquid and bulk rock compositions define approximately parallel trends. Data from Wager and Brown (1967) and Morse (1981). The bulk rock composition with the minimum K_2O concentration for the Kiglapait is clearly anomalous. If it were eliminated, the trends would be coincident as well as parallel, as for the Skaergaard.

APPLICATION TO IGNEOUS SERIES

There are essential differences between magma series involving assimilation and those which do not. Application of these criteria to natural igneous rock series provides informative results. Figure 8 illustrates inferred Skaergaard liquid compositions (Wager and Brown 1967), some thick, fine-grained dolerite sills from Tasmania (McDougall 1962), and the inferred Kiglapait liquid trend (Morse 1981). These are well-documented examples of basaltic fractionation at high levels in the crust where assimilation, particularly assimilation of more mafic material, must have been very minor. Note that they form relatively straight arrays on a magma evolution diagram, despite isotopic detection of small amounts of contamination by continental sediments in the Skaergaard and Kiglapait intrusions (Leeman and Dasch 1978; DePaolo 1985). Figure 9 illustrates the relationship between calculated liquids and rock samples from these two intrusions. Rocks and liquids show trends with a similar

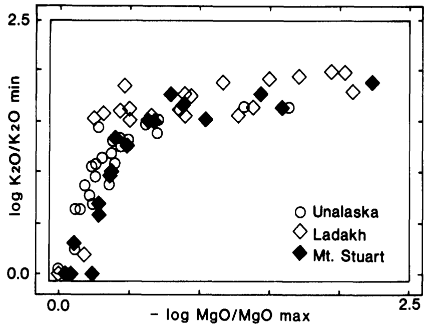

FIG. 10.—Plot of K_2O vs. MgO concentration for calc-alkaline intrusive series where assimilation of mafic rock in more felsic magma has been proposed as an important factor in petrogenesis. Bulk rock compositions plotted are for gabbro through granite; ultramafic rocks are not included. Data from Drewes et al. (1961), Erikson (1977), Perfit et al. (1980), Honegger et al. (1982), and Kelemen and Ghiorso (1986). Although bulk rock compositions do not represent liquid compositions, the three intrusive series form a remarkably consistent trend, distinctly different from the trends of Skaergaard and Kiglapait bulk rock compositions shown in figure 9.

slope; rock compositions show more scatter and larger maxima.

In figure 10, data for three calc-alkaline plutonic series are plotted. Captain's Bay pluton on Unalaska Island in the Aleutian volcanic arc is a zoned gabbro to granodiorite pluton intruding hydrothermally altered, mafic volcanic rock. Drewes et al. (1961) emphasized evidence for assimilation of mafic material along the margin of the pluton by more felsic magma, while Perfit et al. (1980) interpreted chemical variation as the result of crystal fractionation alone. The Mt. Stuart batholith hosts several ultramafic-felsic complexes of varying size and intrudes alpine peridotite lenses which were in amphibolite grade at the time of intrusion. Kelemen and Ghiorso (1986) attributed the ultramafic and gabbroic rocks of the batholith to reaction between quartz-dioritic magma and alpine peridotite. The Ladakh batholith also hosts ultramafic-felsic plutonic complexes, described by Kelemen and Sonnenfeld (1983) as reaction zones between peridotite and felsic magma. The plots for these intrusive suites show a pattern which could be interpreted as the result of combined assimilation and fractional crystallization, and which is certainly distinct from the trends of Skaergaard and Kiglapait rock compositions.

Chemical variation diagrams of intrusive rock series are difficult to interpret since the bulk compositions of the rocks, especially the more mafic examples, do not represent liquid compositions. For this reason, it might be better to plot well characterized volcanic rock series. However, a given volcanic center may include rocks derived from several distinct magma series. Furthermore, more primitive members of a particular fractionation series may not be represented. If fractionation and assimilation proceed rapidly relative to the rate of ascent, then parental melts for some volcanic series may never reach the surface. Where primitive members of magma series do reach the surface, very little assimilation of mantle material is to be expected.

Plots of rocks from subduction-related volcanic centers yield mixed results; some appear to form a straight-line, crystal fractionation trend on the diagrams, and none show the smooth trend formed by the intrusive suites described above. Most common is wide variation in incompatible element concentration in the more magnesian rocks, followed by a trend attributable to crystal fractionation for the more evolved rocks. A typical example, using analyses of Quaternary volcanic rocks from Northeast Japan, is shown in figure 11, and one possible interpretation is shown in the inset. The "noisy" pattern in rocks with high MgO could be due to variable rates of assimilation and variable composition of the assimilate affecting different batches of magma erupted in the same volcanic zone. Alternatively, the pattern could be explained as the result of: (1) fractional crystallization of two or more distinct parental liquids, formed by different degrees of partial melting in the mantle (Masuda and Aoki 1979); (2) magma mixing; (3) partial equilibrium crystallization (a specific case of assimilation of mafic rock combined with fractional crystallization); or (4) combinations of all these processes.

CONCLUSIONS

The effects of combined assimilation and fractional crystallization (*AFC*) in the mantle are similar to those caused by variable degrees of partial melting and those caused by zone refining. However, *AFC* is more general. Whereas partial melts of mantle material

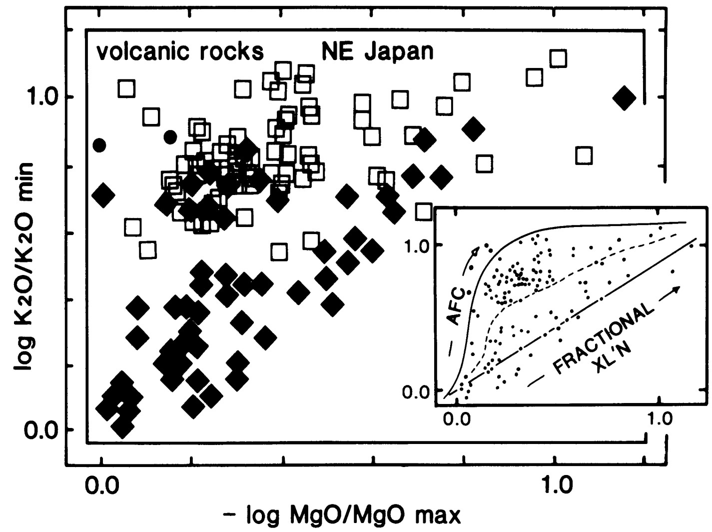

FIG. 11.—Plot of K_2O vs. MgO concentration for Quaternary volcanic rocks of Northeast Japan. Analyses from Kuwano and Aoki (1960), Kuwano et al. (1961), and Yoshida and Aoki (1984). Filled diamonds are for rocks of the tholeiitic series, open squares are for rocks of the calc-alkaline series, and filled circles are for high-alumina basalts; rock classifications, based on petrography, were made by the original analysts. A possible explanation for the pattern formed by the data is sketched in the inset. Variable degrees of assimilation, combined with crystal fractionation, have produced liquids which lie above the fractional crystallization trend defined by the more iron-enriched tholeiitic rocks. Much of the assimilation may have occurred in the upper mantle. Very similar incompatible (Th, K) vs. compatible (Cr, Ni, Mg) element plots for the volcanic rocks of Northeast Japan were presented by Masuda and Aoki (1979). They explained the pattern as the result of fractional crystallization of two or more distinctly different primary magmas, formed by different degrees of partial melting in the mantle.

must have magnesian olivine (ca. Fo90) on the liquidus at the temperature and pressure of formation, mantle *AFC* affects liquids that are not in equilibrium with magnesian olivine. This applies to basalts in their crystallization range at temperatures of about 1300 to 900°C in the upper mantle, whether they are derived from higher temperature regions of the mantle, from compositionally distinct regions in the mantle, or from the underthrust slab in a subduction zone.

Where basaltic magma undergoes fractionation in the upper mantle, and wall rock temperatures approach magmatic temperatures, assimilation of ultramafic rock must occur. This process may be quantitatively important, altering the nature of magmatic arc lithosphere and profoundly influencing the liquid line of descent. Further evaluation of this hypothesis requires field tests in areas with unequivocal evidence of assimilation of ultramafic rock in fractionating magma. Study of plutonic contact zones provides such an opportunity; variation in derivative magma composition may be monitored, in a relative sense, as a function of mineral trace element concentration. This approach could also be used to study xenolith suites from subduction-related volcanic arcs.

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