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Reaction Between Ultramafic Rock and Fractionating Basaltic Magma I. Phase Relations, the Origin of Calc-alkaline Magma Series, and the Formation of Discordant Dunite

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ABSTRACT

This paper presents results of modelling reaction between peridotite and fractionating tholeiitic basalt in simple and complex silicate systems. Reactions are outlined in appropriate binary and ternary silicate systems. In these simple systems, the result of reactions between 'basalt' and 'peridotite' may be treated as a combination of Fe–Mg exchange and mass transfer reactions at constant Fe/Mg. Fe–Mg exchange in ternary and higher-order systems is nearly isenthalpic, and involves a slight decrease in magma mass at constant temperature. Mass transfer reactions, typically involving dissolution of orthopyroxene and consequent crystallization of olivine, are also nearly isenthalpic in ternary and higher-order silicate systems, and produce a slight increase in the magma mass at constant temperature. The combined reactions are essentially isenthalpic and produce a slight increase in magma mass under conditions of constant temperature or constant enthalpy.

Initial liquids saturated in plagioclase + olivine will become saturated only in olivine as a result of near-constant-temperature reaction with peridotite, and crystal products of such reactions will be dunite. Liquids saturated in clinopyroxene + olivine will remain on the cpx–ol cotectic during reaction with peridotite, but will crystallize much more olivine than clinopyroxene as a result of reaction, i.e., crystal products will be clinopyroxene-bearing dunite and wehrlite rather than olivine clinopyroxenite, which would be produced by cotectic crystallization. The Mg/Fe ratio of crystal products is 'buffered' by reaction with magnesian peridotite, and dunites so produced will have high, nearly constant Mg/Fe. Production of voluminous magnesian dunite in this manner does not require crystal fractionation of a highly magnesian olivine tholeiite or picrite liquid.

Combined reaction with ultramafic wall rock and crystal fractionation due to falling temperature produces a calc-alkaline liquid line of descent from tholeiitic parental liquids under conditions of temperature, pressure, and initial liquid composition which would produce tholeiitic derivative liquids in a closed system. Specifically, closed-system differentiates show iron enrichment at near-constant silica concentration with decreasing temperature, whereas the same initial liquid reacting with peridotite produces silica-enriched derivatives at virtually constant Mg/Fe.

Reaction between fractionating basalt and mafic to ultramafic rock is likely to be important in subduction-related magmatic arcs, where tholeiitic primary liquids pass slowly upward through high-temperature wall rock in the lower crust and upper mantle. Although other explanations can account for chemical variation in individual calc-alkaline series, none can account as well for the characteristics shared by all calc-alkaline series. This process, if it is volumetrically important on Earth, has important implications for (Phanerozoic) crustal evolution: sub-arc mantle should be enriched in iron, and depleted in silica and alumina, relative to sub-oceanic mantle, acting as a source for sialic crust. It is probable that inter-oceanic magmatic arcs have basement similar to alpine peridotite, in which sub-oceanic mantle has been modified by interaction with slowly ascending basaltic liquids at nearly

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constant temperature. Discordant dunite bodies in alpine peridotite may record extraction of sialic crust from the Earth's upper mantle.

INTRODUCTION

In this paper, reaction between crystallizing basalt and peridotite will be investigated using graphical analysis of phase diagrams for simple binary and ternary silicate systems, and then using a solution model for natural silicate liquids developed by Ghiorso and others (Ghiorso *et al.*, 1983; Ghiorso, 1985; Ghiorso & Carmichael, 1985). It will be shown that the results of such investigation have important implications for the origin of calc-alkaline vs. tholeiitic magma series, and for the origin of 'replacive' or discordant dunite bodies in peridotite. The graphical analysis has wide application to any system involving reaction of olivine-saturated liquid with lherzolite and harzburgite.

Following Bowen (1922*a*, 1928) and Daly (1914, 1933), the term 'assimilation' is used in this paper to describe any solid–liquid reaction in natural silicate systems which changes the composition of the liquid. By analogy with the terms 'solute' and 'solvent', used in aqueous geochemistry, the noun 'assimilate' is used to describe solid reactants in solid–liquid reaction, and 'assimilant' is used to describe liquid reactants in the same reactions.

Studies of assimilation of felsic material in silicate liquids have become increasingly popular and fruitful in the past few years (e.g., DePaolo, 1981; Grove *et al.*, 1982; Watson, 1982*a*; Huppert & Sparks, 1985; McBirney *et al.*, 1987). Comparatively little attention has been paid to the assimilation of mafic and ultramafic rocks. However, the latter process is probably 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 may often be subject to no such constraint.

As shown by Bowen (1922*a*), solid phases out of equilibrium with a liquid will react with the liquid, regardless of the melting temperature of the pure solid phases. At constant enthalpy, 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*), reaction results in formation of an energetically equivalent mass of saturated phases, the mass produced being larger than the mass consumed. Few subsequent studies of interaction between magma and wall rock have taken a thermodynamic approach, probably because of the scarcity of data on the slope of the multi-component liquidus surface, heats of fusion of solid solutions, and heats of mixing in silicate liquids. Further investigation may also have been discouraged by Bowen's assertion that assimilation processes could not produce liquids fundamentally different from those produced by crystal fractionation alone. Though Bowen showed how assimilation of olivine in liquids could alter the crystal and liquid line of descent, he believed that all such phenomena were of secondary importance, as derivative liquids still can differentiate by crystal fractionation to the same eutectic composition. As emphasis in igneous petrology has shifted from debate over the ultimate destination of liquid fractionation to explanation of the differences between various liquid lines of descent, the potential effect of combined assimilation and crystallization is of increasing interest.

History of the problem

Although less frequently invoked as a petrogenetic process than assimilation of felsic rock, reaction between fractionating magma and refractory wall rock is not a new concept. Apart from the classic treatment of the subject by Bowen (1922*a*), early theoretical discussion includes papers by Harker, Fenner, and Nockolds. Harker (1895, 1900, 1904, 1909) treated the problem theoretically, and his thermodynamic arguments (especially in 1909) in many ways foreshadowed the more detailed discussions of Bowen. Fenner (1920) reported detailed petrographic evidence for reaction of mafic minerals and basaltic glass with felsic magma saturated with lower-melting phases. He noted (Fenner, 1929), perhaps for the first time, that fractional crystallization of basalt would generally produce a trend of iron enrichment, and not silica enrichment, in derivative liquids. He suggested that commonly observed rock series which showed silica enrichment, and little or no iron enrichment, might be formed by reaction between felsic magma and mafic rock. Nockolds (1931, 1932, 1933) was motivated by field evidence for production of intermediate 'hybrid' rocks by reaction between felsic magma and mafic rock. He emphasized the importance of mechanical mixing and grain boundary diffusion through an H_2O-rich medium as mechanisms for mass transfer between crystalline mafic rock and more felsic melts.

More recently, Kays & McBirney (1982) attributed the formation of 'picrite' xenoliths in gabbro in the Skaergaard intrusion to reaction between basaltic melt and wehrlite wall rock. 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 & Wyllie (1982, 1983; Wyllie & Sekine, 1982), and invoked to explain map and outcrop scale contact relations by Ramp (1975), Kelemen & Sonnenfeld (1983), Evans (1985), and Kelemen & Ghiorso (1986). Kelemen and co-workers have also attributed the formation of dunite, hornblendite, and some types of gabbro to reaction between fractionating basaltic liquid and various types of ultramafic rock, as did Hurlbut (1935) in his treatment of mafic inclusions in tonalite. Irving (1980), Menzies *et al.* (1985), Roden *et al.* (1984), and Francis (1987) presented evidence for cryptic and modal metasomatism of spinel lherzolite wall rock by magma in the mantle. Similar relations have been noted in outcrop in alpine peridotite (Ozawa, 1983; Evans, 1985). Several authors, notably Dick (1977*b*) and Quick (1981*a*, *b*), have suggested that some discordant dunite bodies cutting alpine peridotite are formed by reaction between ultramafic wall rock and olivine-saturated basalt.

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. This theory was based on observation of partially resorbed, mantle-derived xenoliths and xenocrysts, and reverse zoning in magmatic hornblende crystals, which suggested that Mg/Fe increased in the melt during crystallization. Largely on theoretical grounds, Kudo (1983) proposed that the calc-alkaline 'hyperthenic' series of Kuno (1950, 1960) was produced by interaction between fractionating tholeiitic magma and mafic amphibolite in the lower crust. Kelemen (1986) and Kelemen & Ghiorso (1986) proposed that assimilation of ultramafic rock in fractionating, mantle-derived olivine tholeiite could produce calc-alkaline derivative liquids under conditions of temperature, pressure, and initial liquid composition which would produce a tholeiitic liquid line of descent by closed-system crystal fractionation. Myers and co-workers (Myers *et al.*, 1985; Myers & Marsh, 1987; Myers, 1988) have argued that high-Fe/Mg, high-alumina basalt, derived by a large degree of partial melting of the downgoing slab in subduction zones, may react with mantle peridotite to produce 'primitive' low-Fe/Mg, high-MgO basalts. Petrographic evidence for reaction between magma and more mafic rocks beneath volcanic arcs, preserved in composite or 'hybrid' xenoliths, has been presented by Conrad *et al.* (1983) and Conrad & Kay (1984).

Takahashi & Kushiro (1983) and Fujii & Scarfe (1985) showed that liquids of differing initial composition, equilibrated with four-phase mantle assemblages (olivine, two pyroxenes and spinel) at 8–10·5 kb and 1225–1300 °C, approached the composition of magnesian mid-oceanic ridge basalts. Falloon & Green (1987) questioned the details of this conclusion, but showed that liquids equilibrated with four-phase assemblages are olivine normative and contain 50 wt. % SiO_2. Stolper (1980) emphasized that, because the primary-phase volume of olivine in basaltic liquids expands with decreasing pressure, many tholeiitic basalts produced by partial melting of four-phase peridotites at higher pressures are strongly undersaturated in orthopyroxene component at 10 kb. Fisk (1986) showed in 1 atm experiments that dissolution of orthopyroxene from mantle wall rock by tholeiitic melts could lead to the metastable formation of high-MgO andesites (boninites). Kelemen *et al.* (1987, 1990) made experiments on mixtures of olivine tholeiite and harzburgite at 5 kb and temperatures (1150–1050°C) below the solidus of the harzburgite and within the melting range for the basalt; liquids produced in basalt–harzburgite mixtures were calc-alkaline whereas those in the basalt alone were tholeiitic.

Most of the present discussion is concerned with reaction between saturated basalt and ultramafic rock. A special case in mantle–magma interaction would arise where a relatively low-temperature liquid, derived from melting in or near the downgoing slab in a subduction zone, interacted with refractory wall rock which was at a higher temperature. Such a situation appears likely when one considers the inverted geothermal gradient above the Benioff Zone which is predicted in virtually all contemporary models for the thermal structure of convergent margins (Hsui & Toksoz, 1979; Anderson *et al.*, 1980; Honda & Uyeda, 1983; Hsui *et al.*, 1983; Tatsumi *et al.*, 1983). Under these conditions, conduction of heat from the wall rock is likely to heat the magma, initially leading to the formation of superliquidus melt. Consequent dissolution of wall rock phases must surely follow, leading to initial cooling of the local mantle-magma system as a result of endothermic reaction, and eventually to formation of a liquid saturated in mantle minerals.

Dissolution of peridotite minerals (magnesian olivine, pyroxenes, spinel and garnet) in superliquidus basaltic liquid has been experimentally investigated by Donaldson (1985), Kuo & Kirkpatrick (1985*a*, *b*), Thornber & Huebner (1985), Brearley & Scarfe (1986), and Tsuchiyama (1986*a*, *b*), who showed that 'linear' dissolution rates, measured at temperatures possibly attained by natural melts in the upper mantle (1400–1200°C), are of the order of 3 m/yr to 3 mm/yr. These rates are very fast, viewed in the context of geologic time and magma residence in the mantle. Zhang *et al.* (1989) suggested that dissolution rates measured in all previous experiments were enhanced by mixing as a result of small-scale convection. They conducted experiments designed to eliminate small-scale convection in the experimental liquid, and measured dissolution rates about two orders of magnitude slower than those previously obtained.

In the absence of detailed knowledge about the mechanism of ascent of basaltic magmas in the mantle, it is difficult to know which data set is most applicable. If melts infiltrate mantle peridotite and percolate upward, then the earlier workers' measurements are probably applicable, whereas if melts ascend as kilometer-scale, discrete diapirs, consisting only of liquid without fragments of residual source material, and wall rock interaction occurs in a nearly static, liquid boundary layer, then the data of Zhang *et al.* may be more applicable. Magma transport in centimeter- to 100-m-scale conduits might be closer to the infiltration case if melt in such conduits moves rapidly and mixes efficiently. Discordant dunite and pyroxenite in alpine peridotite are generally observed on a centimeter- to 10-m-scale, though larger dunite bodies exist.

Using dissolution rates like those obtained by Zhang *et al.*, if ascending melt could remain undersaturated in solids over 100000 yr (Marsh, 1978; Marsh & Kantha, 1978), an initial sphere of magma of 1 km diameter would undergo a 1% increase in radius (500 m initially, plus 100000 yr at 0·05 mm/yr) and a 3% increase in volume. Using likely values for the enthalpy of fusion for mantle minerals (100 cal/g) and the heat capacity of basaltic liquid (0·3 cal/g °C), it can be seen that dissolution of the amount of wall rock involved could cool the magma by about 10 °C (see 'Thermodynamics of solid–liquid reaction in natural systems', below). If, instead, the initial magma body had a 100-m diameter, its volume would increase by 33%, and the dissolution reactions could cool the liquid by 100 °C. Finally, if dissolution rates were 5 mm/yr, as for those measured by workers before Zhang *et al.*, the radius of an initial magma body of 1-km diameter would double, and the volume would increase eightfold! The last two cases are thermodynamically unreasonable. Magmas above their liquidus, residing in the crust or mantle, must eventually become saturated because of the endothermic effect of dissolving wall rock without consequent crystallization, as shown by Bowen (1922*a*) in his well-known critique of hypotheses involving magmatic 'superheat'. Once saturated, however, magmas may dissolve and reprecipitate many times their weight in solid phases without solidifying. Such solid–liquid interaction is the subject of this paper.

Concept and limitations of equilibrium calculations

Throughout this work, it will be implicitly assumed that the effects of reaction between magma and solid inclusions or wall rock, initially out of equilibrium with the magma, can be approximated by a series of equilibrium steps. A good way to visualize this postulate, and to recognize its limitations, is to imagine a chemically homogeneous liquid, out of equilibrium with its wall rocks, in a magma chamber which acts as a closed system except for the periodic addition of stoped blocks. Each block reacts completely with the magma before the next block is added.

In a more realistic mantle–magma system, gradients of composition would exist in both magma and adjacent wall rock. Solid inclusions would be added continuously and, at any given time, some inclusions would be more fully equilibrated with the liquid than others. The solid–liquid interface might not be sharp; liquid might infiltrate the wall rock along grain boundaries (Waff & Bulau, 1979; Bulau & Waff, 1979; Watson, 1982*b*; McKenzie, 1986), and/or a grain boundary film, composed of various rapidly diffusing melt species, might facilitate rapid mass transfer between solid and liquid (Nockolds, 1933). A full treatment of mantle–magma interaction, with these as boundary conditions, would have to consider bewilderingly complex interaction between such poorly understood processes as coupled solid–liquid diffusion, each with concentration-dependent diffusion coefficients; concentration-dependent crystal nucleation, growth, and dissolution, occurring at different rates for different minerals; and magma transport through peridotite at high temperatures and pressures. All these would have to be coupled with a precise knowledge of magma and solid composition, and of the geothermal gradient in the upper mantle, as rates of most of these processes can vary by orders of magnitude as a function of temperature, pressure, and phase composition.

In the absence of a full solution, it is hoped that the heuristic concept of stepwise equilibration will continue to prove useful for some time. In this concept, spatial gradients in temperature, pressure, and composition are divided into sub-systems in which all these variables are initially constant for each phase and the total system, and chemical equilibrium is achieved in each such system without interaction with all others. This approach is likely to approximate the results of mantle–magma interaction for natural systems in which the rate of magma transport is slow relative to the rate of approach to chemical equilibrium, and in which isolated magma 'batches' are homogenized, by mechanical mixing and/or rapid diffusion, but do not interact with other batches of magma.

'Rate' of assimilation vs. crystallization

The limiting factors in assimilation processes include (1) the ratio of mass assimilated to mass crystallized (M_a/M_c) 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. It should be noted that the ratio M_a/M_c can be thought of as a mass balance, or as the integrated ratio of the rate of assimilation (dM_a/dt) divided by the rate of crystallization (dM_c/dt). The crystallization rate is largely a function of the rate of change of temperature. When temperature is constant, the rate of crystallization may be very slow, and equal to the rate of assimilation ($M_a/M_c = 1$). 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.

Under conditions of nearly constant temperature, the constraints outlined above control the mass of mantle wall rock available for reaction with magma but the value of M_a/M_c may be largely determined by equilibrium reaction stoichiometry. Predicting equilibrium M_a/M_c accurately for natural solid–liquid reactions is problematic. As an example, let us consider the reaction

$$\text{low-Ca pyroxene } (\pm \text{ liquid}_1) = \text{Mg-rich olivine} + \text{liquid}_2.$$

As presented by Kelemen (1986) and Kelemen & Ghiorso (1986), calculations made using a solution model for natural silicate liquids (Ghiorso *et al.*, 1983; Ghiorso, 1985; Ghiorso & Carmichael, 1985) predict that the ratio of the mass of pyroxene dissolved to the mass of olivine produced (M_a/M_c) for this reaction at constant temperature in natural magnesian basalts should be ~1·4 (in the temperature range 1300–1100 °C, dissolving En_{90} pyroxene and forming Fo_{89} olivine), corresponding to a molar stoichiometry close to

$$2\ \text{En}\ (MgSiO_3) = 1\ \text{Fo} + 1\ SiO_2\ (\text{liquid}).$$

In the binary Mg_2SiO_4–SiO_2 system at the peritectic reaction point at about 1560 °C, on the other hand, the reaction En = Fo + liquid has stoichiometry close to

$$10\ \text{En} = 1\ \text{Fo} + 1\ SiO_2\ (\text{liquid}) + 8\ MgSiO_3\ (\text{liquid})$$

with $M_a/M_c = 7$ (Bowen, 1922*a*). The large discrepancy between reaction stoichiometry calculated from binary phase relations and that predicted for a natural system is a result of the influence of liquid components other than MgO and SiO_2 on the solid–liquid system. Figure 1 illustrates the lever-rule method by which isothermal reaction stoichiometry in the binary system can be determined, and a similar geometric method for determining reaction stoichiometry in a ternary system involving forsterite, silica, and a third, unspecified oxide component. In Fig. 2, contours are shown for solutions using this method, in a generalized ternary diagram in which the unspecified third oxide component is denoted MO.

Application of this general diagram in determining isothermal reaction stoichiometry in the ternary forsterite–anorthite–silica system is also shown in Fig. 2. On the forsterite–anorthite cotectic, as in the forsterite field, the effect of isothermal assimilation of pyroxene would be the formation of forsterite. M_a/M_c would be ~1·2, as in the forsterite field immediately adjacent to the cotectic. Even in this ternary system, displacement of the liquid composition from the forsterite–SiO_2 join changes the peritectic reaction stoichiometry so that it is very nearly equal to that predicted for natural, multi-component systems.

Consideration of the likely stoichiometry for similar reactions in natural systems, and their effect upon the liquid line of descent, forms the main emphasis of this paper. We will concentrate mainly on those reactions likely to be important in the reaction of fractionating

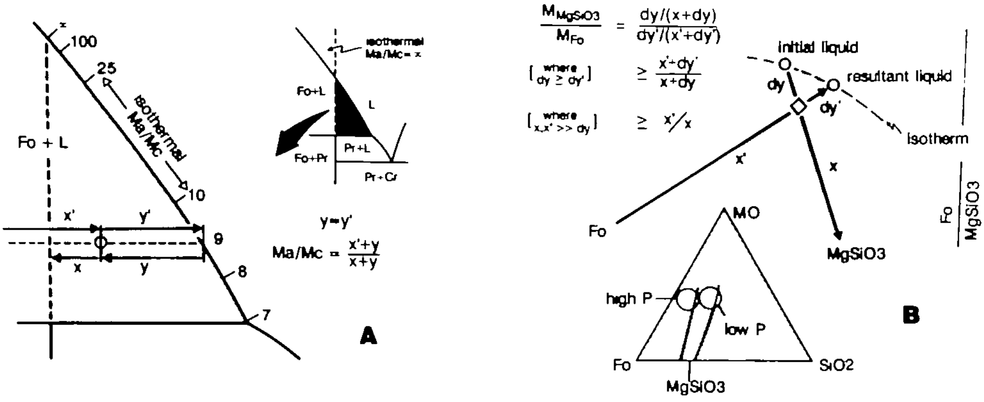

FIG. 1. Graphical methods for determining stoichiometry of the reaction (clino)enstatite = forsterite + liquid at constant temperature. (Mass forsterite/mass enstatite = M_a/M_c). Fo: forsterite; Pr: proto-enstatite; L: liquid; Cr: cristobalite. (A) In the binary Mg_2SiO_4–SiO_2 system, the composition of liquid saturated with $MgSiO_3$ is isothermally, isobarically invariant. By the lever rule, the mass enstatite 'assimilated'/mass forsterite produced (M_a/M_c) is equal to $y/(x+y)\cdot(x'+y')/y'$, and, as $y=y'$, $M_a/M_c=(x'+y')/(x+y)$. (B) In ternary systems with components Mg_2SiO_4 (Fo), SiO_2, and an arbitrary third component, MO, the ratio M_a/M_c can be estimated at constant temperature using the lever rule, provided: (1) both pyroxene consumed and olivine formed lie on the high-temperature side of the isotherm; and (2) 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.

olivine tholeiite and lherzolite, namely: (1) reactions which consume magnesian olivine plus liquid to form more iron-rich olivine, and (2) reactions which consume low-calcium pyroxene to produce liquid plus olivine (± calcic pyroxene). Before more detailed discussion of specific reactions, however, a general discussion of the thermodynamics of solid–liquid reactions in natural silicate systems will be given.

Thermodynamics of solid–liquid reaction in natural systems

Bowen (1922*a*) observed that the enthalpy change during assimilation reactions at constant temperature can be approximated by the difference between the heat of fusion of the solid phases consumed by reaction and the heat of crystallization of phases produced. This is true because heats of mixing in natural silicate liquid systems are negligible in comparison with the heats of fusion of most silicate minerals. Unlike the dissolution of salts in aqueous solution, which can evolve heat without consequent crystallization, the pure dissolution of most silicate minerals (except possibly SiO_2 polymorphs; Ghiorso & Kelemen, 1987) is endothermic.

Dissolution of refractory phases in liquids in equilibrium with less refractory phases in the same reaction series (defined in Bowen, 1922*b*), at constant temperature, causes crystallization of the phases with which the magma is saturated (Bowen, 1922*a*). This process maintains the composition of the liquid on the isothermal liquidus surface. The mass crystallized will be larger than the mass of the refractory phase 'dissolved', and Bowen suggested that such reactions would generally be exothermic. Bowen also developed examples of assimilation of less refractory phases in liquids saturated with higher-temperature phases in the same reaction series. In these examples, the mass of crystals produced by reaction is less than the mass consumed.

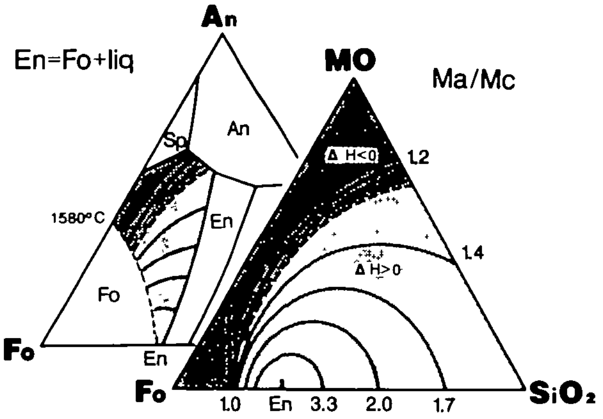

FIG. 2. *A generalized ternary system with components Mg_2SiO_4, SiO_2, and an unspecified third component,* denoted MO. The ternary diagram is contoured for minimum estimated values of the ratio of mass enstatite (En) consumed to mass forsterite (Fo) produced (M_a/M_c) in the reaction En = Fo + liquid ($dy \geq dy'$; see Fig. 1). The dashed contour marks the isenthalpic stoichiometry: calculated enthalpy change is greater than zero for $M_a/M_c > 1{\cdot}29$ at 1400 °C, $M_a/M_c > 1{\cdot}33$ at 1000 °C. Along this contour, reaction will produce no temperature change in systems closed to heat transfer, provided the reactants are at the same initial temperature. For $M_a/M_c > 1{\cdot}33$ reactions will absorb heat, cooling the system if it is closed to heat transfer. The contours are valid only within the forsterite field in any specific system; as an illustration, the pertinent contours are shown in the system Fo–SiO_2–anorthite (An) determined by Anderson (1915). It should be noted that the low-Ca pyroxenes in this and any other Ca-bearing system may not lie in the ternary plane, and certainly are slightly displaced from $MgSiO_3$ on the Fo–SiO_2 join. However, displacements have a very minor effect in this application. In iron-bearing systems, specialized ternary diagrams could be constructed for olivine–SiO_2–MO, where the olivine composition is that produced by the equilibrium low-Ca pyroxene = olivine + liquid. Again, the low-Ca pyroxene composition is unlikely to be significantly displaced from the ternary plane or the olivine–SiO_2 join, and the contours for M_a/M_c should be in very similar locations. An exception, when the low-Ca pyroxene phase is pigeonite, is unlikely to occur in reactions between mantle peridotite and fractionating basalt. Natural silicate liquids in equilibrium with magnesian olivine (± plagioclase) will plot very near the isenthalpic reaction contour.

Bowen also briefly discussed constant-temperature assimilation across a cotectic ‘valley’, which results in dissolution without consequent crystallization, a necessarily endothermic process. This applies to assimilation of a refractory phase in liquid saturated in another refractory phase which is not in the same reaction series; for example, to assimilation of forsteritic olivine in liquid saturated with anorthite-rich plagioclase. In the examples, it was shown that the energy required to dissolve the assimilate could not normally be provided by the heat capacity of the magma, as heats of fusion for silicates are generally two to three orders of magnitude larger than heat capacities of silicate liquids, per gram. Bowen estimated that heat capacities of natural silicate liquids were of the order of 0·2–0·3 cal/g °C, and heats of fusion of mafic silicates were close to 100 cal/g. Subsequent research has upheld these estimates (Ghiorso & Carmichael, 1980; Stebbins *et al.*, 1984). Bowen reasoned that in natural systems, the results of dissolving a low-melting member of one reaction series will normally be a drop in temperature, followed by crystallization of a smaller mass of the phase(s) in another reaction series with which the magma is saturated.

Assimilation of a refractory phase in liquid saturated with a less refractory phase in the same reaction series, at constant temperature, need not always be exothermic. Similarly, assimilation of a low-melting phase in magma saturated with a higher-melting phase in the same reaction series need not be endothermic. Instead,

$$\Delta H = M_a \cdot \Delta H_f^a - M_c \cdot \Delta H_f^c$$

for M_a equal to the mass assimilated, M_c equal to the mass crystallized, and H_f^a and ΔH_f^c equal to the apparent heats of fusion, per gram, of the assimilate and the resultant crystals, respectively. Apparent heats of fusion are the heats of fusion of the solids at some temperature, T', below the melting temperature of the pure solid, T_m. They may be calculated as

$$\Delta H_f = \Delta H_F + \int_{T'}^{T_m} C_{p_{\mathrm{solid}}}\,\mathrm{d}T - \int_{T'}^{T_m} C_{p_{\mathrm{liquid}}}\,\mathrm{d}T$$

where ΔH_f is the apparent heat fusion of the pure solid at T', ΔH_F is the heat of fusion of the pure solid at its melting temperature, T_m is the melting temperature of the pure solid, and $C_{p_{\mathrm{solid}}}$ and $C_{p_{\mathrm{liquid}}}$ are the integrated heat capacities of the pure solid and a liquid component of the same composition over the temperature range $T_m - T'$. The magnitude and sign of the total enthalpy change in a solid–liquid reaction may vary, depending on the ratios M_a/M_c and $\Delta H_f^a/\Delta H_f^c$.

The ΔH for constant-temperature assimilation of a low-melting phase in magma saturated with a more refractory phase in the same reaction series will often be very close to zero, because, although M_a/M_c in such reactions must generally be greater than one, as shown by Bowen (1922*a*), the apparent enthalpy of fusion of the low-melting assimilate will generally be smaller than the apparent enthalpy of fusion of the refractory equilibrium crystal assemblage. For example, let us take the assimilation of low-calcium pyroxene in a liquid saturated with magnesian olivine. At 1200 °C, the apparent heats of fusion of forsterite and (clino)enstatite are ~170 and 130 cal/g, respectively [heats of fusion, melting temperatures, and solid and liquid heat capacities from Robie *et al.* (1979), Ghiorso & Carmichael (1980), and Stebbins *et al.* (1984)]. Contours of the approximate stoichiometry for such reactions, for the generalized ternary system forsterite–SiO_2–MO, are shown in Fig. 2. Likely values of M_a/M_c for natural silicate systems range from 1·2 to 1·4, so that the resultant enthalpy change at 1200 °C ranges from -14 to $+12$ cal/g pyroxene dissolved. These very small enthalpy changes bracket the isenthalpic reaction stoichiometry ($M_a/M_c \cong 1{\cdot}3$).

During isothermal assimilation of a less refractory phase, or assimilation of material across a cotectic 'valley' (assimilation of a phase in a reaction series with which the magma is not saturated), ΔH will always be positive. For instance, assimilation of forsterite in liquid saturated with anorthite at constant temperature in the system forsterite–diopside–anorthite (Osborn & Tait, 1952) must always be endothermic. The process of dissolving forsterite will move the liquid composition off the anorthite liquidus surface. There will be no limit to the enthalpy change produced by such isothermal reaction at 1300 °C until the liquid is saturated in forsterite. Until then, ΔH will increase by 190 cal/g forsterite dissolved (ΔH_f for forsterite at 1300 °C). If a reservoir of anorthite is initially present in the system, dissolution of forsterite at constant temperature will lead to dissolution of anorthite as well.

Constant temperature is generally an unreasonable constraint for assimilation of phases across a cotectic valley. During such endothermic reactions, magmatic temperature cannot often be buffered at a constant value. If, instead of constant temperature, the system were constrained to constant enthalpy, then the temperature would drop. The condition of constant enthalpy, in general, requires that

$$\Delta T = [M_a \cdot \Delta H_f^a - M_c \cdot \Delta H_f^c] / M_{\mathrm{tot}} \cdot C_{p_{\mathrm{tot}}}$$

where M_{tot} is equal to the total mass of the system and $C_{p_{\mathrm{tot}}}$ is the heat capacity of the system (~0·3 cal/g °C, assuming that the masses of the solids in the system are small, or that $C_{p_{\mathrm{solid}}}$ is approximately equal to $C_{p_{\mathrm{liquid}}}$). For assimilation across a cotectic valley, ΔT must always be less than zero.

The foregoing discussion applies to dissolution and consequent crystallization where the assimilate is at magmatic temperature before reaction. Where this is not the case, the energy required to heat the assimilate to magmatic temperature must also be included in the calculation of mass and energy balance at constant temperature or constant enthalpy. Again, Bowen treated this problem. He noted that the heat of crystallization of saturated phases can supply the energy needed to heat inclusions, or wall rock, or both. Because the heats of fusion of silicate minerals are orders of magnitude greater than heat capacities of silicate minerals, per gram, crystallization of a mass of liquid can raise the temperature of an equivalent mass of solids by 100 °C or more.

Calc-alkaline magma series

Fenner (1929) may have been the first igneous petrologist to point out that, whereas well-known examples of differentiation of basaltic magma by crystal fractionation showed a trend of iron enrichment, many igneous rocks, including the large batholiths of the western USA, showed a trend of silica enrichment accompanied by little or no iron enrichment in differentiates. We now know the iron-enrichment trend as 'tholeiitic' and the silica-enrichment trend as 'calc-alkaline' (Fig. 3). [For a history of this terminology, and the rigorous definitions adopted by most petrologists today, see Irvine & Baragar (1971).]

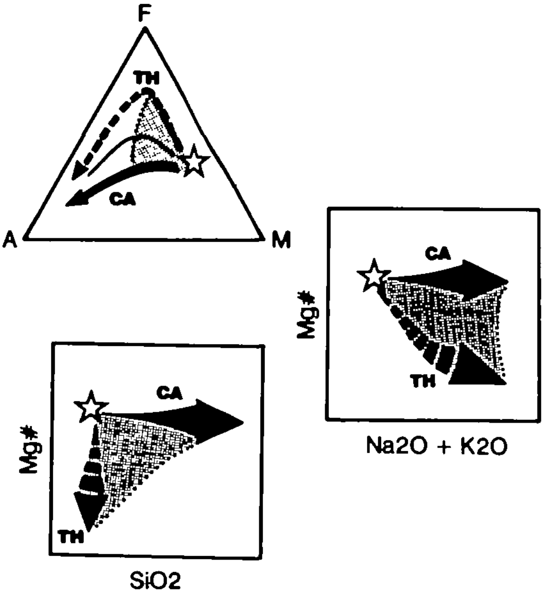

FIG. 3. Generalized illustration of chemical variation in tholeiitic (TH) and calc-alkaline (CA) igneous series. All chemographic diagrams in weight per cent. A = $Na_2O + K_2O$, F = $FeO + 0{\cdot}9Fe_2O_3 + MnO$, and M = MgO. The *mg*-number (Mg #) = MgO/(MgO + total Fe as FeO). It should be noted that *mg*-number can be constant or increasing even when MgO content of the liquid is decreasing. Whereas calc-alkaline series are found almost exclusively in subduction-related magmatic arcs, tholeiitic series are found at both convergent and divergent plate boundaries.

Fenner proposed that the tholeiitic trend was the normal result of crystal fractionation from basalt, an idea which was later supported by the analysis of the Skaergaard layered intrusion by Wager & Deer (1939). It has become evident that, whereas tholeiitic magma series are found at convergent and divergent plate margins, and are represented among within-plate magma types as well, calc-alkaline series are virtually restricted to igneous rocks formed at convergent plate margins (Gill, 1981).

The calc-alkaline 'problem', as posed by Fenner, is that most ferromagnesian silicates formed from cooling basaltic magma have higher Mg/Fe ratios than coexisting magma. Where the crystallizing assemblage involves substantial proportions of plagioclase, the solids may contain a lower absolute concentration of Fe as well. These facts appear to lead inevitably to iron enrichment (decreasing Mg/Fe, and possibly increasing total Fe) in liquid series derived from basalt by crystal fractionation. Similarly, many pyroxenes and plagioclases have as much or more silica than coexisting basalt, so that silica enrichment is not a general consequence of crystal fractionation involving these phases.

Rocks in some calc-alkaline series may be produced by partial melting of rocks which are compositionally distinct from the mantle source for tholeiitic melts. For example, some calc-alkaline tonalites may be produced by partial melting of amphibolites in the lower crust (Beard & Lofgren, 1987). However, many volcanic and plutonic suites at consuming plate margins exhibit continuous variation in liquid and rock compositions, from olivine tholeiite to evolved dacites; it is possible that these suites are derived by differentiation of a common parental liquid. In the interest of brevity, we shall simply take this possibility as a likelihood, and review proposed processes for differentiation. Grove and others (Grove *et al.*, 1982; Grove & Baker, 1984; Grove & Kinzler, 1986) have recently reviewed explanations for the calc-alkaline liquid line of descent, assuming it is derived from a tholeiitic parent. These are summarized below with additional references provided for those interested in the history of this problem:

(1) Some calc-alkaline series, such as that in the Lesser Antilles, may be largely controlled by early hornblende (+olivine+plagioclase, etc.) fractionation. Hornblende has Fe/Mg only slightly greater than that of coexisting basalt, and SiO_2 contents less than that of basalt. Early advocates of this hypothesis include Best & Mercy (1967), Takeshita & Oji (1968*a*, *b*), and Cawthorn & O'Hara (1976).

(2) Even less iron-enriched series may result from mixing of evolving basalt with a crustal partial melt or from combined assimilation of crustal wall rock and fractional crystallization. This idea may have originated with Holmes (1932), and was extensively developed by Kuno (1950). Some indisputable examples of this process exist (Wilcox, 1954; Grove *et al.*, 1982; McBirney *et al.*, 1987). Kelemen (1988) has shown, however, that equilibrium assimilation of pelitic wall rock, and of dry granitic rock or liquid, cannot produce a calc-alkaline trend under conditions of temperature, pressure, and initial liquid composition which would produce a tholeiitic liquid line of descent in a closed system. Calc-alkaline trends can be produced where the assimilate is a hydrous granitic melt.

(3) Effects similar to those expected for (2) may be produced by magma mixing involving highly evolved and extremely mafic members of the same fractionation series, as argued by Wager & Deer (1939), Eichelberger (1975), Anderson (1976), and Sakuyama (1978, 1981, 1983).

(4) Additionally, although their theory was not explicitly included by Grove and others, we should include the hypothesis of early magnetite fractionation, induced by conditions of relatively high oxygen fugacity, as suggested by Kennedy (1948, 1955), Osborn (1959), and many subsequent workers. This hypothesis is implicitly invoked by all workers who model

calc-alkaline series as the result of anhydrous crystal fractionation, usually involving some combination of olivine (±orthopyroxene) + clinopyroxene + plagioclase + magnetite. Early formation of magnetite is necessary to such hypotheses, as it lowers the Mg/Fe ratio and the total SiO_2 concentration in the crystallizing assemblage.

All these theories for the genesis of calc-alkaline magma series have their adherents, and there can be no doubt that each of the processes described above does operate in the igneous environment at some places and times. Furthermore, as several such processes may often occur in conjunction, and as their compositional effects as expressed in derivative liquids are rather similar, it may prove difficult to isolate the 'driving force' responsible for a particular igneous series. However, it would be elegant, though not necessary, if a single process always produced those features which uniquely characterize calc-alkaline series: a relative lack of iron enrichment accompanied by early enrichment in silica and alkalis.

As mentioned above, Kelemen and co-workers (Kelemen, 1986, 1987; Kelemen & Ghiorso, 1986; Kelemen *et al.*, 1987, 1990) have proposed that calc-alkaline series may be formed where tholeiitic basalt reacts with ultramafic wall rock under conditions of temperature, pressure, oxygen fugacity, and initial magma composition which would produce a tholeiitic liquid line of descent in a closed system. It is not the intent of this paper to provide a critique of the other four theories enumerated above, but instead to provide a detailed description of this simple process, capable of producing calc-alkaline rock series, which must operate to some extent in every case where magma generated at depth passes through high-temperature ultramafic and mafic wall rock.

Discordant dunite

Discordant dunite bodies occur in peridotite, pyroxenite, and gabbro from layered intrusions, in pyroxenite and wehrlite from concentrically zoned ultramafic–felsic and ultramafic–mafic plutonic complexes, and in lherzolite and harzburgite in ophiolites and alpine-type peridotite. The present discussion will concentrate on the characteristics of discordant dunite in ophiolites and alpine peridotite. The dunite bodies to be discussed are discordant in the sense that they crosscut model banding and/or a pre-existing foliation in peridotite. In addition to smaller bodies, dunite in the 'transition zone' (Coleman, 1977; Nicolas & Prinzhofer, 1983) between tectonite peridotite and cumulates in ophiolites commonly crosscuts local structures in the peridotite. Discordant dunite typically includes chromian spinel and small amounts of plagioclase, clinopyroxene, and/or orthopyroxene. Transition zone dunites, in particular, are often associated with, and gradational into, wehrlite 'cumulates' (Himmelburg & Loney, 1980; Boudier & Coleman, 1981; Hopson *et al.*, 1981; Nicolas & Prinzhofer, 1983; Ozawa, 1983, 1984). Similar associations of discordant dunite and wehrlite occur in contact zones where mafic plutons have been emplaced in harzburgite or lherzolite wall rock (Quick, 1981*a*).

Particularly interesting is that some dunite bodies are demonstrably replacive of lherzolite and/or harzburgite host rocks. A replacive origin is demonstrated where dunite bodies crosscutting modal banding or pyroxenite dikes do not offset these features (e.g., Dick, 1977*a*, *b*; Dungan & AveLallement, 1977; Nicolas & Prinzhofer, 1983) or where peridotite inclusions within anastamosing dunite bodies clearly have decreased in size so that, if the intervening dunite were removed, they would no longer 'fit' the surrounding walls (Fig. 4). Both Boudier & Nicolas (1977) and Quick (1981*b*) have even reported the presence of spinel-rich pyroxenite dikes in the host rock which are cut by discordant dunite, but persist as continuous spinel trains within the dunite body. Such detailed evidence shows that little if

FIG. 4. Discordant dunite 'dikes' or 'veins' cutting pyroxenite (websterite) in the Big Jim plutonic complex, a concentrically zoned, ultramafic–felsic plutonic complex in the Washington Cascades, described by Kelemen & Ghiorso (1986). It should be noted that the anastamosing dunite encloses relict pyroxenite 'islands' whose outline would not match the adjacent walls if the dunite were removed. These contact relations suggest that some of the dunite formed by near constant volume replacement of pyroxene by olivine. Field of view 3 m wide.

any volume change accompanied replacement of peridotite by dunite, but this cannot often be demonstrated in a particular outcrop.

Several potentially complementary theories for the origin of discordant dunite in peridotite have been offered:

(1) Partial melting *in situ* consumed most of the orthopyroxene, as well as clinopyroxene and plagioclase, leaving a residue of olivine and chrome spinel (Boudier & Nicolas, 1972, 1977; Dick, 1977*a*,*b*; Jackson & Ohnenstetter, 1981; Nicolas & Prinzhofer, 1983).

(2) The bodies are 'cumulate dikes' which were originally channels for the migration of olivine-saturated melts and were eventually filled by the crystal products of these magmas (Aho, 1956; Ruckmick & Noble, 1959; Moores, 1969; Loney *et al.*, 1971; Himmelburg & Loney, 1973; Menzies & Allen, 1974; Dick, 1977*a*,*b*; George, 1978; Harkins *et al.*, 1980; Boudier & Coleman, 1981; Hopson *et al.*, 1981; Quick, 1981*a*,*b*; Nicolas & Jackson, 1982; Nicolas & Prinzhofer, 1983).

(3) Some replacive dunites are 'pyrometamorphic' products, formed by localized partial melting of wall rock by very hot magmas passing though adjacent dikes (Boudier & Nicolas, 1972, 1977; Dick, 1977*a*,*b*; Boudier & Coleman, 1981).

(4) The dunite bodies were formed by incongruent dissolution of pyroxene and/or plagioclase in H_2O-rich fluid at high temperature (Bowen & Tuttle, 1949; Aho, 1956; Heckroodt, 1959; Hess, 1960; Cameron & Desborough, 1964; Irvine, 1974; Dungan & AveLallement, 1977; Himmelburg & Loney, 1980; Schiffries, 1982; Raedeke & McCallum, 1984; Kelemen & Ghiorso, 1986).

(5) An idea similar to (4) is that replacive dunites may be formed when H_2O-undersaturated, pyroxene-saturated magma undergoing crystal fractionation becomes sufficiently rich in H_2O to stabilize olivine and dissolve pyroxene (Kelemen & Ghiorso, 1986). A phase diagram which illustrates this possibility for a simple silicate system has been presented by Kushiro (1972*a*, fig. 2).

(6) Replacive dunite bodies may be formed by incongruent dissolution of pyroxene and/or plagioclase during reaction between wall rock and magma saturated only in olivine and spinel (Dick, 1977*b*; Hopson *et al.*, 1981; Quick, 1981*a*,*b*; Reuber, 1985). At first glance,

this hypothesis seems rather similar to the suggestion that dunite bodies originate by partial melting of peridotite. Among authors who have written of partial melting of peridotite wall rock by magma passing through adjacent dikes some, for instance Boudier & Nicolas (1977), suggested that these melts must have been at temperatures near 1400 °C, whereas others may have meant to specify a process of magma–wall rock interaction at somewhat lower temperatures.

(7) Finally, replacive dunite may be formed by incongruent dissolution of pyroxene and/or plagioclase during reaction between peridotite and silicate liquid even when the liquid is initially a multiply saturated, tholeiitic melt (Kelemen, 1987). Such reactions, as well as forming dunitic reaction zones in wall rock, will eventually remove plagioclase (and possibly clinopyroxene) from the liquidus of the derivative magma, leaving a liquid saturated only in olivine ± chrome spinel. In other words, olivine cumulate bodies need not have been formed by primary picritic liquid derived from great depth, or by large degrees of partial melting of peridotite *in situ*. They may be cumulates from multiply saturated tholeiitic liquid which has been contaminated by extensive reaction with peridotite wall rock.

It seems probable that all the processes described above do operate at specific places and times in the upper mantle, and obvious that different processes may have been dominant in the formation of different discordant dunite bodies. In a general way, one can assess the nature of the processes which formed specific dunite bodies by comparing the composition of olivine (and/or spinel) in dunite and host rock. Figure 5 is a plot of reported forsterite content in olivine from dunite bodies vs. forsterite content in olivine from peridotite associated with these bodies.

If most dunite in ophiolites and alpine peridotite had been formed by *in situ* partial melting of a peridotite host, then one would expect the olivine in dunite to be consistently more magnesian than olivine in host peridotite. On the other hand, if most dunite bodies had been formed by fractional crystallization from picritic magma, then one would expect to see a trend of iron enrichment in the cumulate dunites, and the compositional range of the olivine in the dunites should be much larger than that in host peridotite. Although the data presented are permissive of small amounts of partial melting and/or fractional crystallization in individual cases, in general the range of compositions is almost identical for dunite and peridotite from the same complex. There is a tendency for olivine in dunites to be slightly more iron-rich than olivine in peridotite, but no olivine in host or dunite is more iron-rich than Fo_{85}.

It is difficult to explain this limitation to magnesian compositions in terms of fractional crystallization. Observation of a limited range of olivine composition in discordant dunite is consistent with extensive reaction between magma and host, forming olivine-rich reaction products whose composition was 'buffered' by the refractory, magnesium-rich olivine in the wall rock. To understand this process we must investigate two types of reaction: (1) equilibria between magnesian olivine and liquid saturated in more iron-rich olivine, and (2) dissolution of low-calcium pyroxene in magma initially saturated in olivine ± calcic pyroxene and/or plagioclase.

GRAPHICAL ANALYSIS OF PHASE DIAGRAMS

Reaction between Mg-rich olivine and liquid

To demonstrate a hypothesis for the formation of calc-alkaline liquid series and discordant dunites, we now turn our attention to phase diagrams for simple silicate systems.

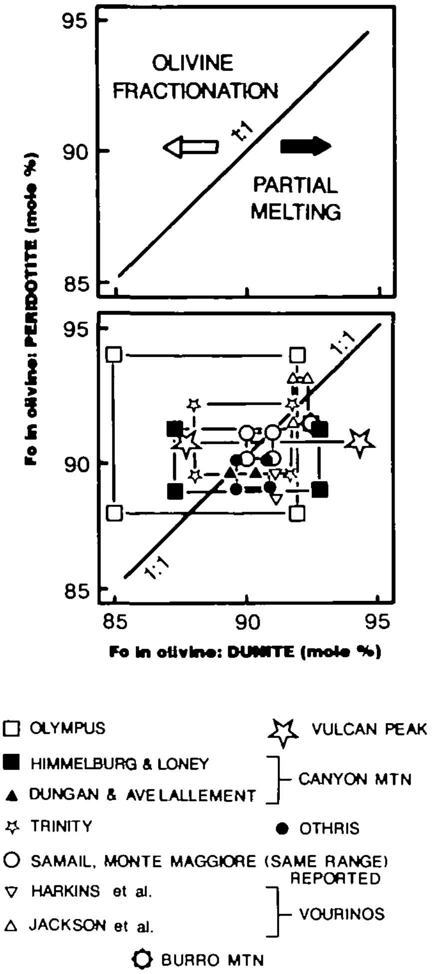

FIG. 5. Comparison of olivine compositions in discordant dunite and peridotite (harzburgite, lherzolite, and wehrlite) hosts from alpine peridotite bodies and ophiolites. The upper graph shows the expected trend of composition if discordant dunites were formed by olivine fractionation from a basaltic melt, or by partial melting of the peridotite host. The lower graph summarizes values from the literature. Care has been taken to avoid analyses of olivine in cumulate layers above the 'transition zone' in ophiolites. In most cases, reported analyses represent 'average' or 'typical' compositions for all discordant dunite and peridotite from a specific complex. Rectangles connecting points represent the reported range of olivine composition in both dunite and peridotite, and adjacent dunite–host pairs could potentially lie anywhere within the rectangle. Only in a few cases (Boudier & Coleman, 1981; Quick, 1981*b*) were analyses obtained from immediately adjacent dunite and host. Data from: George (1978), Olympus; Himmelburg & Loney (1973), Vulcan Peak; Dungan & AveLallement (1977) and Himmelburg & Loney (1980), Canyon Mountain, Quick (1981*a*,*b*), Trinity; Menzies & Allen (1974), Othris; Boudier & Coleman (1981) and Hopson *et al.* (1981), Samail; Jackson & Ohnenstetter (1981), Monte Maggiore; Jackson *et al.* (1975) and Harkins *et al.* (1980), Vourinos; Loney *et al.* (1971), Burro Mountain.

As these systems perforce have fewer components than natural rocks and magmas, this analysis will address the nature of magma–mantle interaction by parts. This section is designed to illustrate the effect of equilibration between wall rock with magnesian olivine and magma saturated in more iron-rich olivine on the composition and proportion of phases in the magma–wall rock system. For brevity, such equilibria will be referred to as

Fe–Mg exchange reactions, though they do involve net mass transfer (from liquid to olivine), unlike exchange reactions in the terminology of metamorphic petrology.

The system forsterite-fayalite

The analysis will begin with the forsterite-fayalite (Fo–Fa) system originally determined by Bowen & Schairer (1935). Their phase diagram is reproduced as Fig. 6. Let us suppose that 50 g of crystals of olivine with 86 wt.% forsterite (90 mol % forsterite) is immersed in 50 g of liquid at 1605 °C in the Fo–Fa binary which is just saturated with an infinitesimal amount of olivine with 73 wt. % forsterite (Fo_{80}). In Fig. 6, the new bulk composition created in this way is illustrated as a circle. We neglect, for the moment, the unreasonable temperatures at which such an experiment would have to be conducted. At constant temperature, the effect of changing the bulk composition in this way is crystallization of ~69 g Fo_{80}. Of the initial 50 g of liquid, only 31 g remains.

In the parlance of modern literature on assimilation, the mass Fo_{90} assimilated/mass Fo_{80} crystallized (M_a/M_c) during this reaction is 0·72. This ratio is useful because it is independent of the amounts of reactants (50 g each in the case discussed) and only requires knowledge of the compositions of the liquid assimilant (~40 wt.% Fo, or Fo_{49}), the assimilate (86 wt.% Fo, Fo_{90}), and the crystals formed (73 wt.% Fo, Fo_{80}). In any such binary system, M_a/M_c at constant temperature is equal to the difference in forsterite content (weight fraction) between the liquid and the crystals formed, divided by the difference between the liquid and the assimilate (Bowen, 1922*a*; Kelemen, 1986; also see Fig. 1):

$$M_a/M_c = (73-40 \text{ wt.\%})/(86-40 \text{ wt.\%}) = 0{\cdot}72.$$

Recasting the isothermal 'experiment' in terms of end-members, the net result of reaction is

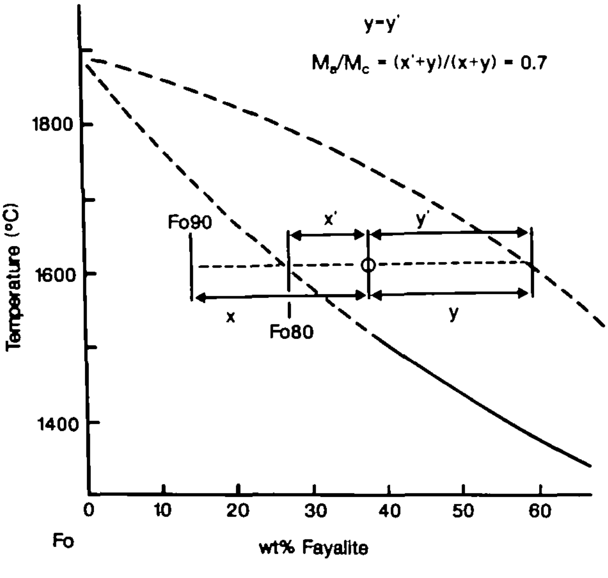

FIG. 6. A part of the binary system Fo–Fa, after Bowen & Schairer (1935). The reaction of magnesian olivine [90 mol % forsterite (Fo_{90})] with liquid saturated in more iron-rich olivine [80 mol % forsterite [Fo_{80})] is illustrated. The ratio of mass Fo_{90} dissolved to Fo_{80} crystallized in such a reaction is the distance from the liquid composition to the saturated-phase composition divided by the distance from the liquid composition to the 'assimilated'-phase composition. The bulk composition discussed in the text is shown as a circle.

the crystallization of 7 g of forsterite and 12 g of fayalite. Such a reaction is exothermic, and evolves 3·3 kcal, or 33 cal/g olivine + liquid in the system.

What if the same experiment were done under conditions of constant enthalpy? In a system closed to heat transfer, the energy input from the exothermic reaction would increase the temperature and dissolve some of the olivine in the system, causing both liquid and olivine to become more magnesian. An approximate estimate of the resulting temperature can be made using thermodynamic data for the olivine end-members and assuming ideal mixing in both liquid and solid solutions. Heats of fusion of the pure end-members at their melting temperatures are about 290 cal/g for Fo at 1890 °C and 110 cal/g for Fa at 1217 °C. The heat capacities of pure, solid Fo and Fa (metastable) in the temperature range 1650–1600 °C are ~0·35 and 0·25 cal/g K, respectively. The heat capacities of the end-member liquids are ~0·45 cal/g K for Fo and 0·28 cal/g K for Fa (Robie *et al.*, 1979; Ghiorso & Carmichael, 1980).

A much smaller mass of more magnesian olivine is formed in response to assimilation of Fo_{90} olivine in an Fo_{49} liquid under isenthalpic conditions than at constant temperature. At 1640 °C, the apparent enthalpies of fusion are ~265 and 123 cal/g for Fo and Fa, respectively. The equilibrium assemblage at this temperature is 47 g liquid, with 46 wt. % forsterite (Fo_{55}), and 53 g olivine, with 77 wt. % forsterite (Fo_{83}). The net effect of reaction is to dissolve ~2 g of forsterite and form 5 g of fayalite, and so, within the rather wide limits imposed by the inaccuracy of the phase diagram and the estimates for the apparent enthalpies of fusion, the reaction is isenthalpic. For this case, $M_a/M_c = 0{\cdot}94$.

Forsterite, fayalite and an arbitrary third component

Returning to the isothermal case, M_a/M_c for small increments of isothermal assimilation in a ternary system can be approximated by the distance from liquid to assimilate divided by the distance from liquid to solid reaction products, as shown in Fig. 1. In natural systems involving Fo, Fa and a complex 'third component', it is clear that liquids in equilibrium with olivine will be substantially displaced from the Fo–Fa join. For instance, in Fig. 7, natural basalts in equilibrium with olivine are shown in a weight per cent ternary diagram in which all liquid components apart from Fo and Fa plot at the third 'MO' apex. Figures 8A–C are contoured in M_a/M_c for the reactions in which an infinitesimal amount of Fo_{90}, plus liquid, forms Fo_{80} (A), Fo_{85} (B), and Fo_{65} (C). Natural liquids in equilibrium with Fo_{65}, for example, plot between the contours for M_a/M_c equal to 0·75 and 0·9 in (C). In (A), the contours are valid for liquids in equilibrium with olivine close to Fo_{80}. For these melts, minimum M_a/M_c is between 0·90 and 0·95. In general, M_a/M_c should be $>0{\cdot}75$, <1, and proportional to both temperature and Mg/(Mg + Fe) in olivine-saturated, natural basaltic liquids reacting with magnesian olivine in the mantle. Furthermore, reaction stoichiometries in natural systems will generally be slightly exothermic, but very close to the isenthalpic value, illustrated as a dashed line in Figs. 8A–C. Thus, the ratio mass assimilated to mass crystallized in such reactions, and the temperature, would be almost identical under both isothermal and isenthalpic conditions.

Figure 9 shows isothermal liquid fields in the ternary system Fo–Fa–MO; as liquids are constrained to remain along a given isotherm, the effect of constant-temperature reaction between olivine-saturated magma and magnesian olivine in this system is to produce a progressively smaller mass of liquid with progressively higher Mg/(Mg + Fe). It should be noted that this effect is mainly due to addition of iron to the solid phase, combined with a relatively minor increase in the concentration of Mg in the derivative liquid. Over the compositional range considered, the ratio of mole per cent MgO in olivine/MgO in liquid [denoted *D*(MgO) ol/liq] remains roughly constant at constant temperature, as noted by

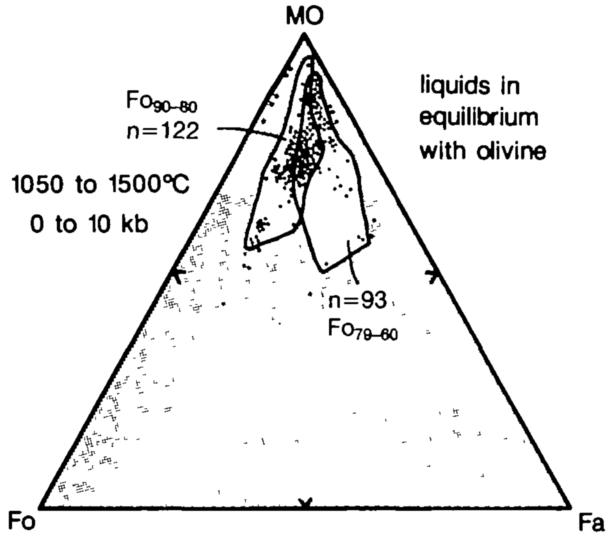

FIG. 7. Compositions of natural silicate liquids in equilibrium with olivine, compiled from experimental data by Ghiorso *et al.* (1983), plotted on a ternary chemographic diagram whose apices are forsterite, fayalite, and an arbitrary third component, denoted MO. Ferric/ferrous iron ratios for the liquids, at the reported oxygen fugacities of the experiments, were calculated by the method of Kilinc *et al.* (1983). Then forsterite was formed from all MgO plus an appropriate mass fraction of SiO_2, and fayalite was formed from all FeO (not total Fe) plus an appropriate mass fraction of SiO_2. The mass fractions of remaining SiO_2, plus Fe_2O_3 and all other oxides, were summed to make MO. A total of 242 compositions are plotted, of which 122 were in equilibrium with Fo_{90-80} olivine, and 93 were in equilibrium with Fo_{79-60} olivine.

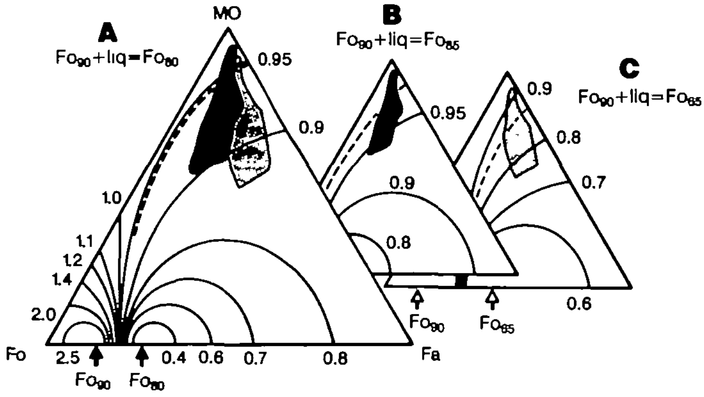

FIG. 8A, B & C. Ternary chemographic diagrams, with components forsterite, fayalite, and an arbitrary third component, denoted MO, constructed as shown in Figs. 1 and 2. The diagrams are contoured in terms of the estimated mass assimilated vs. mass crystallized for constant-temperature reactions between magnesian olivine and liquids saturated in more iron-rich olivine ($dy \cong dy'$; see Figs. 1 and 9). The fields of liquids in equilibrium with two ranges of olivine composition (from Fig. 7) are shown as shaded areas: Fo_{90-80}: dark pattern; Fo_{79-60}: light pattern. In each ternary, a dotted line indicates the stoichiometry of isenthalpic reaction, where the apparent heat of fusion of the magnesian olivine consumed is equal to the apparent heat of fusion of the more iron-rich olivine produced. Reaction is endothermic for M_a/M_c greater than the isenthalpic value, and exothermic for M_a/M_c less than the isenthalpic value. These isenthalpic reaction stoichiometries are nearly constant over the temperature range 1400–1000 °C. It should be noted that natural liquids in equilibrium with olivine generally fall below but near the isenthalpic contour in all three diagrams; even in systems closed to heat transfer, reaction between magnesian olivine and liquid saturated in more iron-rich olivine will involve little change in temperature, provided that the reactants are at the same initial temperature.

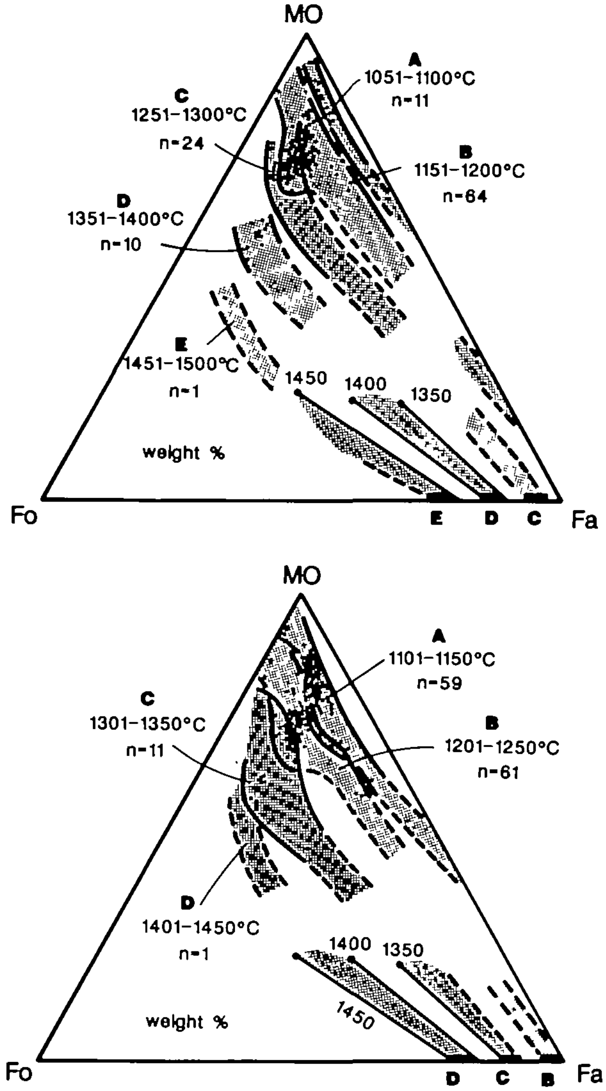

FIG. 9. Natural silicate liquids in equilibrium with olivine, at 0–10 kb and 1050–1450 °C, plotted on the ternary chemographic diagram Fo–Fa–MO (all other oxides) in weight per cent. (See caption for Fig. 7 for further explanation.) Here, fields have been constructed by enclosing all liquid compositions in equilibrium with olivine in a given temperature range. Additional data along the Fo–Fa join, and the liquidus curves labelled 1350, 1400, and 1450 (°C) are for the system FeO–MgO–SiO_2, from Bowen & Schairer (1935). Isotherms in these diagrams approximate lines of constant mol % MgO in olivine/MgO in liquid. This relationship holds if the activity coefficients for silica, FeO, and magnesia components in the liquid are constant over the entire compositional range of liquids (Longhi *et al.*, 1978), which is approximately true over the range of liquid compositions produced by reaction between mafic basalt and magnesian olivine in the mantle. This diagram can be used as a graphical geothermometer, to calculate the equilibrium temperature to about ± 50 °C, particularly useful where liquid compositions are reported in the literature, and the liquid is known to have been in equilibrium with olivine, but no other compositional information is available.

Roeder & Emslie (1970). A slight increase in MgO concentration in the liquid will occur as olivine becomes more magnesian at constant *D*(MgO). For instance, *D*(MgO) ol/liq at 1050 °C is predicted to be ~9·05 (Roeder & Emslie, 1970) for 'dry' basaltic liquids. This corresponds to ~5·8 mol % MgO in liquid saturated in Fo_{80} olivine, and 6·6 mol % MgO in liquid saturated in Fo_{90} (1·1 times more than the 'initial' value). Iron content, on the other hand, changes drastically. *D*(Fe) is estimated to be about 2·86 at 1050 °C, corresponding to 4·6 mol % FeO in liquid in equilibrium with Fo_{80} and 2·3 mol % FeO in liquid saturated in Fo_{90} (half the 'initial' value).

Fe–Mg exchange reaction between liquid and two-pyroxene lherzolite, for liquids saturated in ortho- and/or clinopyroxene as well as olivine, would be generally similar in its effect to Fe–Mg exchange between liquid and olivine alone. Assimilated and product pyroxene will be more magnesian than assimilated and product olivine, respectively. M_a/M_c and enthalpy change in all such reactions will be very similar to that predicted for olivine alone in similar ranges in Mg/(Mg + Fe) of the liquid and solid phases. To summarize, the effect of isothermal or isenthalpic reaction between basalt, in equilibrium with relatively iron-rich olivine and/or pyroxenes, and wall rock containing more magnesian members of the same solid solutions, will be a slight decrease in the total liquid mass of the system and an increase in Mg/(Mg + Fe) in the derivative magma.

Assimilation of lherzolite in tholeiitic basalt in the systems Fo–SiO_2–An, Fo–SiO_2–Di, and Fo–Di–An

Fractionating liquids, passing through cooler wall rocks in the upper mantle, will usually not be multiply saturated in two pyroxenes, olivine, and garnet, spinel, or plagioclase. It has been shown in general that partial melts formed from 'four-phase peridotite' (olivine, two pyroxenes, and spinel) at 10–30 kb will be saturated only in olivine at lower pressures, and will fractionate toward clinopyroxene and/or plagioclase saturation (e.g., O'Hara, 1965, 1968; Stolper, 1980; Elthon & Scarfe, 1980, 1984). In particular, Stolper (1980) has shown that many tholeiitic liquids at 10 kb and below are very far from orthopyroxene saturation. Walker *et al.* (1979) have emphasized that most mid-oceanic ridge tholeiites are saturated in olivine + plagioclase + calcic pyroxene, and this may be taken to be a likelihood for partial melts of mantle peridotite which have ascended to the uppermost mantle while fractionating olivine. The upper mantle is generally considered to be composed primarily of chrome spinel-bearing, olivine-rich harzburgite and lherzolite. Thus, reaction between fractionating mantle melts and mantle wall rock at pressures less than the pressure of melting is likely to involve reaction between liquid undersaturated in low-calcium pyroxene and a wall rock containing substantial amounts of low-calcium pyroxene.

Dissolution of pyroxene in melt saturated only in olivine (± Cr-spinel) was predicted by Quick (1981*b*), who briefly discussed the probable effect on the composition of the derivative magma using a projection onto the Fo–Di–SiO_2 phase diagram devised by Walker *et al.* (1979). Fisk (1986) experimentally demonstrated metastable effects of orthopyroxene dissolution in olivine-saturated liquid. This section will elaborate on several important aspects of the equilibrium topology of such reactions, which were not treated by either Walker *et al.* or Fisk. The mass and composition of derivative liquids are predictable using simple phase diagrams. During assimilation of some kinds of peridotite, magmas become richer and richer in silica until they are saturated in orthopyroxene. This could be the source of the many small orthopyroxenite dikes found in the ultramafic sections of many ophiolites and in alpine peridotite bodies. Assimilation of other types of peridotite produces only olivine (± chrome spinel) plus liquid indefinitely, regardless of the masses of solid and liquid reactants involved, a process capable of forming voluminous, magnesian dunite. Perhaps most importantly, the consequences of assimilation of peridotite in liquid initially saturated in plagioclase and/or clinopyroxene, as well as olivine, are similar to the consequences when the initial liquid is saturated only in olivine.

Constant temperature

To address these questions, examples will be presented in the simple ternary systems Fo–SiO_2–An (anorthite), Fo–SiO_2–Di (diopside) and Fo–Di–An. Each of these systems has rather similar topology, for our purposes, and most of the discussion will be illustrated by use of the Fo–SiO_2–An ternary only, the choice being determined by the relative abundance of mantle-derived, relatively primitive basalts saturated in both olivine and plagioclase at low to moderate pressure. Figure 10 is a reproduction of the phase diagram for Fo–SiO_2–An, determined by Anderson (1915), cast in mole per cent of the three components. Assimilation of lherzolitic wall rock at constant temperature in this system can be represented by increments of 'dissolution' of lherzolite in the magma, followed by increments of crystallization. Dissolution forms a metastable, supersaturated liquid composition which lies beneath the liquidus surface in temperature–composition space; crystallization moves the liquid back to the isothermal liquidus surface. Figure 11A illustrates the same relationship on a weight per cent diagram.

Assimilation of wall rock at constant temperature is an end-member process which is unusual in the crust, but relatively likely in the mantle. Unlike basaltic magmas in the crust, basalts in the upper mantle may ascend sufficiently slowly through the mantle that they remain at nearly the same temperature as their wall rocks, and still remain liquid. In the upper mantle, temperatures will generally be well below the liquidus of primary partial melts of peridotite, without being below the solidus of fractionating basaltic magma. Thus, initially constant temperature across the magma–mantle interface is a likely boundary condition at the outset of solid–liquid reaction. If heat conduction is rapid relative to the rate of reaction, and/or the enthalpy change due to reaction is small, then constant temperature could be

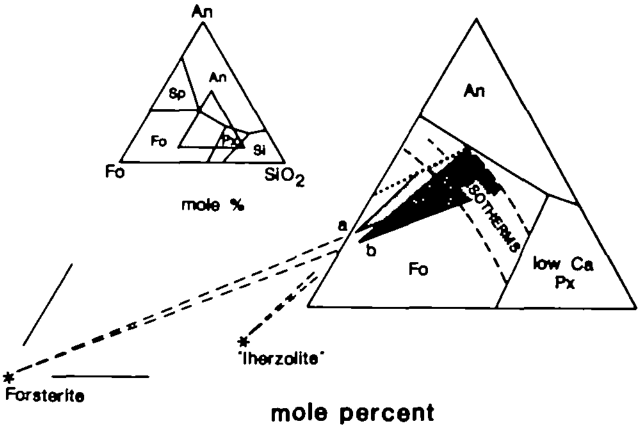

FIG. 10. A portion of the system Fo–SiO_2–An, determined by Anderson (1915). Other abbreviations for solid phases used in this and following figures are Sp for spinel and Px for low-Ca pyroxene. Assimilation of a simple system lherzolite in 'haplobasaltic' liquid at constant temperature is depicted in terms of (metastable) steps of dissolution of lherzolite, and consequent crystallization of olivine returning the liquid to the isothermal liquidus surface. Case (a) is for assimilation of lherzolite in liquid saturated only in Fo. Case (b) is for a more evolved liquid, saturated in both Fo and An. In both cases, isothermal assimilation of lherzolite produces a liquid saturated only in Fo.

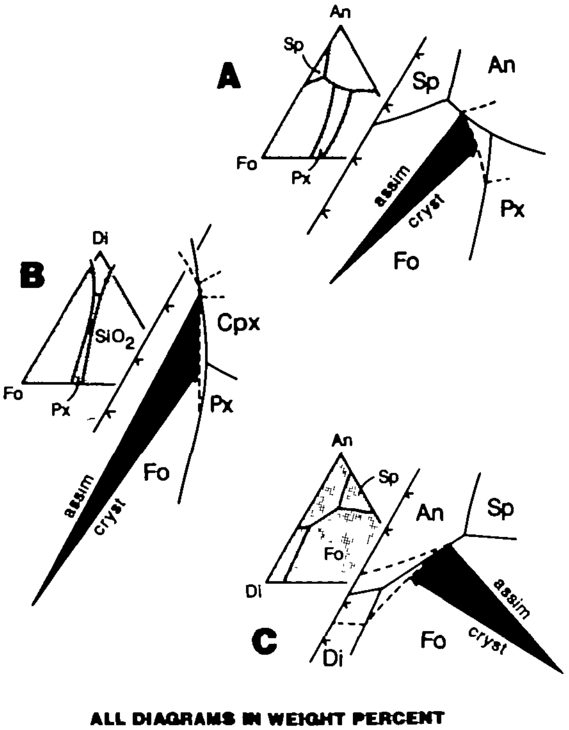

FIG. 11. Assimilation of simple lherzolite compositions in multiply saturated liquids, depicted in: (A) Fo–SiO_2–An from Anderson (1915); (B) Fo–SiO_2–Di determined by Bowen (1914) and revised by Kushiro (1969, 1972*b*); and (C) Fo–Di–An, investigated by Osborn & Tait (1952). In addition to previously defined abbreviations, Cpx is used to refer to calcic pyroxene. All these phase diagrams are for systems at 1 atm, and are in weight per cent. However, although the sizes of the Fo and An stability fields decrease with increasing pressure, the basic topology of reactions within the Fo stability field and along bounding cotectics does not vary significantly with pressure. In all the cases illustrated, isothermal assimilation of lherzolite or harzburgite in multiply saturated liquid produces a liquid saturated only in Fo.

maintained throughout the reaction process. In any case, isothermal mantle–magma interaction provides an end-member process with which we can compare reaction under conditions of falling (or rising) temperature, isenthalpic reaction, and/or changing pressure.

Consideration will be given primarily to isothermal assimilation of ‘model lherzolite’ in multiply saturated ‘model basalt’. Assimilation of simpler ‘model harzburgite’, and assimilation into liquids saturated only in olivine, are special cases; their consequences can easily be seen in the discussion of the most general type of reaction. However, one caveat is essential: in the low-pressure phase diagrams used, the ‘model lherzolites’ are metastable with respect to olivine, pyroxene, and melt. In iron- and alkali-free systems, ‘lherzolite’ compositions fall within the stability field of forsterite plus liquid. It is impossible to depict a ‘basaltic’ melt, saturated in olivine + plagioclase and/or calcic pyroxene, which is below the minimum melting temperature of a model lherzolite. Unlike the model lherzolites, model harzburgite or model wehrlite would be solid under the conditions illustrated. One way to rationalize the relationships depicted here is that they are part of a stepwise approach toward equilibrium. The first step in this process is to create metastable olivine, pyroxene, and liquid which all have the same FeO/MgO ratio so that they fall on a ternary phase diagram like those depicted in Figs. 10–15. The next step is to react these metastable phases at constant Fe/Mg, and the final step is to return the new phase assemblage to heterogeneous equilibrium via Fe–Mg exchange. The complete process is illustrated schematically in Fig. 12.

In the isothermal case illustrated in Fig. 10, an increment of dissolution of the model lherzolite in liquid saturated in forsterite creates a liquid supersaturated in forsterite, and not anorthite, even though the lherzolite contains some of the anorthite component. Even if the liquid reactant is initially saturated in anorthite as well as forsterite, assimilation produces a liquid saturated only in forsterite; crystallization moves the liquid composition back to the isothermal liquidus surface, but does not return it to the forsterite–anorthite cotectic. The exact composition of the assimilate chosen, even if it is pure harzburgite or enstatite, does not affect these steps in the reaction process, as long as it lies on the 'uphill' side of the isothermal liquidus, and on the SiO_2-rich side of the forsterite–liquid tie-line.

These relationships have exact parallels in the systems Fo–SiO_2–Di and Fo–Di–An. In Fo–SiO_2–Di (Fig. 11B), determined by Bowen (1914) and revised by Kushiro (1972*b*), isothermal assimilation of model lherzolite in liquid saturated in Fo + Di moves the liquid off the Fo–Di cotectic and into the olivine field. Again, the composition of the assimilate need only lie on the silica-rich side of the Fo-liquid tie-line and on the 'uphill' side of the isotherm, to produce this effect. For instance, the assimilate could be an Fo + En mixture (or even pure En at low pressure) without any Di component. In Fo–Di–An (Fig. 11C), determined by Osborn & Tait (1952), isothermal assimilation of model lherzolite ($Fo_{80}An_5Di_{15}$) in (Fo + An)-saturated liquid again moves the liquid off the cotectic and into the olivine field. As in the other ternaries, this effect will occur whether the assimilate is a 'lherzolite', an Fo + Di 'wehrlite', or an 'olivine pyroxenite'. Assimilation of Fo + Di, Fo + An, or Fo + Di + An mixtures rich in Fo, in (Fo + Di)-saturated liquid will have a similar effect, moving the liquid into the Fo field along an isotherm.

Having examined the three planes which bound the Fo field in the quaternary system Fo–Di–An–SiO_2, we can conclude that isothermal assimilation of a solid assemblage in the Fo field, in any cotectic liquid composition bounding the Fo field (except liquids on the Fo–En field boundary), can result in the crystallization of Fo only, and can produce a derivative liquid saturated only in Fo. Even under conditions of decreasing temperature, melts initially in the Fo field which react with 'peridotite' will generally reach the bounding cotectics at lower temperatures than the same melts crystallizing in a closed system.

Reaction stoichiometry

Before investigating how this line of reasoning might be extended to natural systems, it will be useful to consider the details of the simple system reactions more closely. Figure 13 illustrates the incremental steps of isothermal assimilation of a model lherzolite ($Fo_{80}An_5Si_{15}$) in the system Fo–SiO_2–An. Because the ratio M_a/M_c for small increments of reaction progress is equal to the the length of the liquid–forsterite tie-line divided by the length of the liquid–lherzolite tie-line (see Fig. 1), and because the liquid–forsterite tie-line must always be longer than the liquid–lherzolite tie-line, we can deduce that M_a/M_c will always be greater than one. This reasoning applies equally well to assimilation of model harzburgite ($Fo_{90}Si_{10}$) in the same liquid, even though the temperature of this solid–liquid reaction is well below the harzburgite solidus. It is perhaps easier to understand this process if it is couched in terms of breakdown of pyroxene to form olivine plus liquid, although this occurs well below the melting temperature of the pyroxene on its own composition.

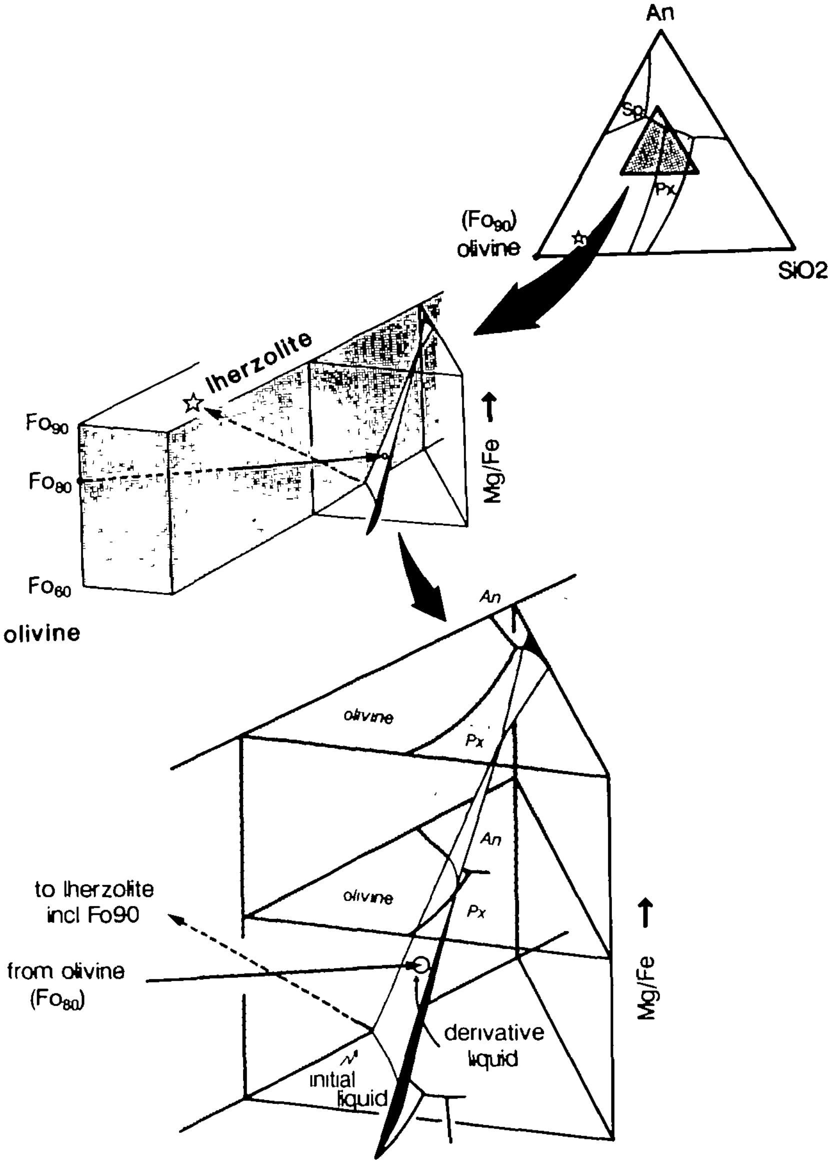

FIG. 12. Schematic illustration of the effect of isothermal reaction between melt and magnesian lherzolite in the system olivine–An–SiO_2. Lherzolite (star), including Fo_{90} olivine, reacts with a liquid lying in the plane Fo_{60}–An–SiO_2. At the temperature chosen, magnesian lherzolite is well below its solidus, whereas the initial basaltic liquid is just saturated in olivine and plagioclase. A small increment of reaction produces Fo_{80} olivine plus liquid with higher Mg/Fe (circle), saturated only with olivine. This reaction process may be separated into two parts, Fe/Mg exchange between lherzolite and liquid, and mass transfer involving dissolution of pyroxenes and crystallization of additional olivine. Figures 6–9 illustrate Fe/Mg exchange reactions, and Figs. 2 and 10–16 refer to the mass transfer reactions. Fe/Mg exchange combined with mass transfer is treated explicitly in Fig. 17, and reaction between basalt and peridotite in natural multicomponent systems is illustrated in Figs. 18–22.

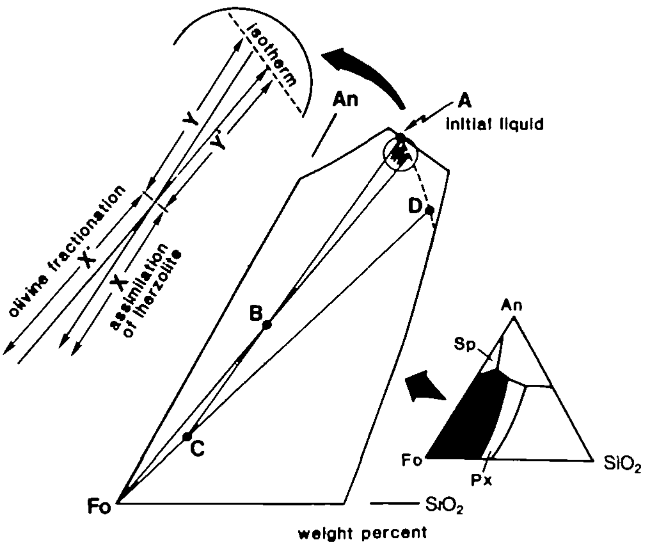

FIG. 13. A graphical method for calculating mass assimilated vs. mass crystallized, for isothermal assimilation of lherzolite in the system Fo–SiO_2–An (Anderson, 1915). For small increments of reaction, the mass assimilated vs. mass crystallized is equal to the distance from the liquid composition to Fo (X') divided by the distance from the liquid composition to the lherzolite (X), as the increments of composition change due to 'dissolution' (Y) and crystallization (Y') are very small and nearly equal in length (mass) on a weight per cent diagram ($dy \geq dy'$; see Fig. 1 and text for further explanation of lever-rule calculations). It can be seen that M_a/M_c will always be greater than one, as, for any assimilate in the Fo stability field, $X' > X$. In the case illustrated, liquid initially saturated in Fo + An moves along the isothermal liquidus into the Fo stability field as a result of reaction. Furthermore, as assimilation proceeds, the bulk composition of the system approaches that of lherzolite (from A to B to C), and the composition of the liquid moves along the isothermal liquidus surface from A to D. Each mass increment of reaction leads to a smaller change in the liquid composition. In the limit, the lherzolite composition forms Fo plus liquid of composition D. In other words, in the iron-free system illustrated, the lherzolite is metastable with respect to Fo + liquid D. In natural systems, magnesian lherzolite would be stable as a solid assemblage, but would react in an analogous way with a more iron-rich liquid initially saturated in olivine plus plagioclase, with additional effects due to Fe–Mg exchange. (See Fig. 12.)

Enthalpy change

It should be noted that, even though the reactions described in this section generally produce more liquid than they consume, they are not necessarily endothermic. Let us consider an example in which assimilation of a small mass of Fo + En at constant temperature results in the crystallization of a smaller mass of Fo, and the formation of more liquid in the system. M_a/M_c for the incongruent breakdown of En has already been illustrated in Fig. 2, the ternary system Fo–SiO_2–MO. The reaction is isenthalpic when the mass of En consumed is $\sim 1{\cdot}3$ times greater than the mass of Fo produced. As long as M_a/M_c in such a reaction remains $< 1{\cdot}3$ but $> 1{\cdot}0$, the reaction will be exothermic even though it increases the mass of liquid in the system. This is true because the apparent enthalpy of fusion of forsterite (per gram) is so much larger than the apparent enthalpy of fusion of enstatite. [However, please see note added in proof, p. 93.]

What happens when the assimilate is harzburgite or lherzolite, rather than pure En? Let us consider Fig. 14, in which 40 g harzburgite with 30 wt. % En + 60 g liquid initially saturated in Fo + An react at 1300 °C to form 37 g Fo + 63 g liquid. In this particular case (bulk composition A), the overall M_a/M_c is $\sim 1{\cdot}1$. However, the stoichiometry of the reaction

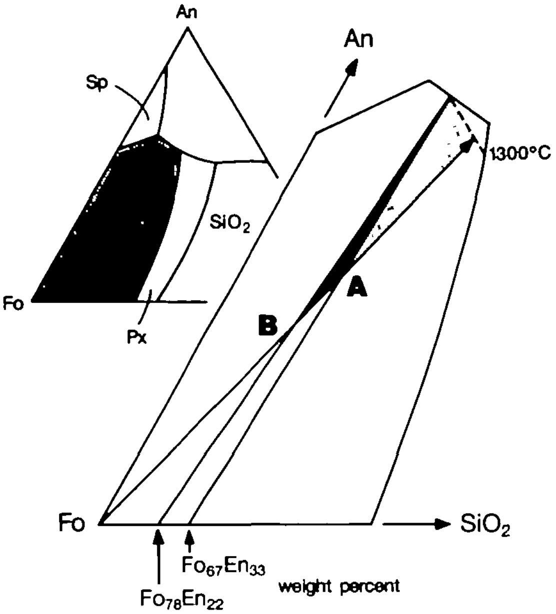

FIG. 14. A portion of the system Fo–SiO_2–An, determined by Anderson (1915). The diagram provides a basis for graphical, lever-rule calculations of stoichiometry and enthalpy change for isothermal reactions between basaltic liquid and harzburgite, as discussed in the text. The initial liquid is saturated with Fo+An. Two different harzburgite compositions at 1300 °C are used to produce bulk compositions A and B. Reaction between basalt and harzburgite, in both cases illustrated, produces an identical derivative liquid composition in the Fo stability field. Reaction in bulk composition A is approximately isenthalpic, whereas reaction in bulk composition B is slightly endothermic. (See text for further discussion.)

involving incongruent breakdown of En is masked by the equilibrium condition

$$\mathrm{Fo} + \mathrm{liquid} = \mathrm{Fo} + \mathrm{liquid}$$

with $M_a/M_c = 1$. If we isolate the En breakdown reaction, we find that dissolution of 12 g En produces 9 g Fo, with $M_a/M_c = 1{\cdot}3$. Thus the En breakdown reaction, in this case, is approximately isenthalpic. If reaction with a more olivine-rich assimilate produced the same liquid composition (bulk composition B), 50 g harzburgite (39 g Fo and 11 g En) + 50 g initial liquid = 45 g Fo + 55 g liquid, the total M_a/M_c is still equal to 1·1, M_a/M_c for the En breakdown reaction is 1·8, and the reaction is endothermic. (For comparison, lherzolite and harzburgite, comprising >75% of the large Trinity alpine peridotite body in northern California, contain 70–80% olivine, 15–20% orthopyroxene, 1–10% clinopyroxene, 1–2% chrome spinel, and 2–10% plagioclase; Quick, 1981*a*).

In all the examples developed in ternary systems thus far, the phases involved (other than Fo) have apparent enthalpies of fusion (per gram) approximately equal to that of enstatite at the same temperature. Furthermore, the fairly reasonable (olivine-rich) model lherzolite compositions used include <33 wt. % En, An, and/or Di component. For these reasons, one can deduce that the model reactions illustrated are all slightly endothermic. In a system closed to heat transfer, they would cause a small decrease in temperature, and in some cases the phase relations discussed would be significantly different from those described for the constant-temperature case. In iron-bearing systems, however, the exothermic effect of

'Fe–Mg exchange' reactions (discussed above) must be considered in an overall evaluation of mass and heat balance in mantle–magma reaction.

Reaction products: *dunite*, *orthopyroxenite*

Until this point, features of magma–lherzolite reaction which are common to virtually any lherzolite, harzburgite, or wehrlite composition have been emphasized. However, if the process of assimilation continues indefinitely, the ultimate destination of the derivative liquid is a function of the composition of the assimilate. Figure 15 illustrates this, again making use of the phase diagram for Fo–SiO_2–An. The position of the assimilated lherzolite relative to the Fo–liquid tie-line, and to the line joining Fo and the point where the isothermal liquidus meets the Fo–Px field boundary, determines the course of the liquid composition during reaction.

Isothermal assimilation of compositions lying in region (1) results in the dissolution of low-Ca pyroxene, and the crystallization of a large mass of olivine and a smaller mass of anorthite (+spinel). When the wall rock assemblage lies in region (2) in Fig. 15, the liquid composition will leave the Fo–An cotectic (at low pressure) or the Fo–Sp cotectic (at high pressure) and move along an isotherm until it lies along the extension of the Fo–lherzolite tie-line. At this point, the liquid composition will remain fixed (at constant temperature) and continued assimilation of lherzolite will simply produce more Fo and more liquid. This is also the case illustrated in Fig. 13.

Isothermal reaction between the same liquid and compositions lying in region (3) causes the liquid composition to move gradually along the isotherm from the Fo–An cotectic to the Fo–Px field boundary. Once there, the liquid composition remains fixed. For the case

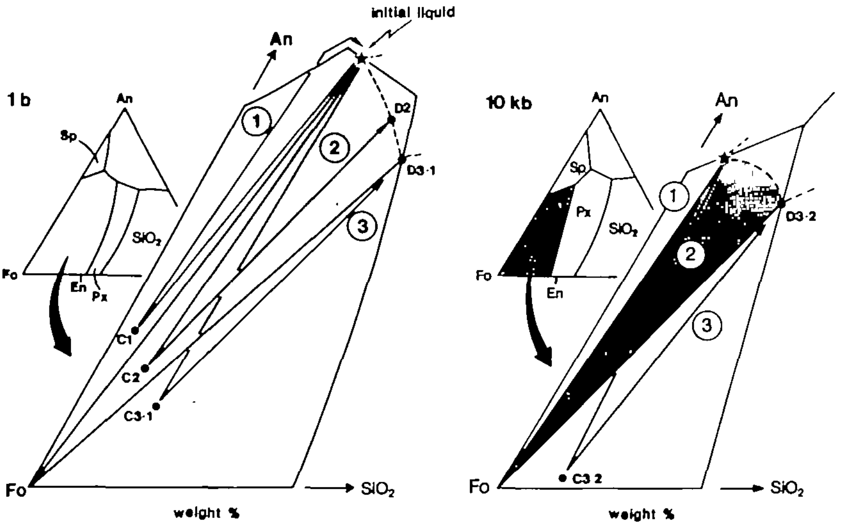

FIG. 15. Portions of the system Fo–SiO_2–An at 1 b and 10 kb (Anderson, 1915; Chen & Presnall, 1975; Presnall *et al*., 1979) illustrating the three possible topologies for isothermal reaction between liquid saturated in Fo+An and a simple system lherzolite or harzburgite in the Fo stability field. Initial liquid composition is indicated by a star. Points C1–C3 are compositions of model lherzolites and harzburgites lying in regions (1)–(3). Points D2 and D3 are the limiting liquid compositions produced by reaction between initial liquid and an infinite mass of peridotite with composition C2 and C3, respectively. In the cases illustrated at 1 b, D2 is reached only at the limit, whereas D3-1 would be reached by derivative liquids after 4 parts peridotite (C3-1) were added to 1 part initial liquid. At 10 kb, D3-2 would be reached by derivative liquids after 2 parts peridotite (C3-2) were added to 1 part initial liquid. (See text for further discussion.)

illustrated in the 1-b phase diagram, ~400 g of lherzolite composition C3-1 would have to be added to 100 g of initial liquid before the derivative liquid reached the Fo–Px field boundary. In the 10-kb diagram, ~200 g of the harzburgite composition C3-2 would have to be added to 100 g of initial liquid before the derivate liquid was saturated in orthopyroxene. It is clear that basalt–peridotite reactions, when the periodotite composition lies in the natural analogues of regions (2) and (3), are capable of producing voluminous discordant dunite, even when the initial basalt is not 'picritic'.

In region (3), continued isothermal assimilation in liquid on the Fo–low-calcium pyroxene peritectic at low pressure will produce low-Ca pyroxene (close to En in composition), dissolving all other phases in the lherzolite. At higher pressure (above ~2–5 kb, e.g., Chen & Presnall, 1975; Presnall *et al.*, 1979) liquid on the Fo–Px field boundary in this ternary system is saturated with Fo + low-calcium pyroxene. If the assimilate is a low-calcium pyroxene + Fo mixture, then assimilation will effectively cease. If the assimilate is lherzolite, M_a/M_c will continue to be greater than one, and the mass of magma in the system will increase, since the An component in lherzolite, which is not included in Fo or low-C pyroxene, will be incorporated in the liquid. It should be noted that, although Fo and An do not coexist stably in this ternary above about 5 kb (Presnall *et al.*, 1979), the same lines of reasoning still apply to assimilation of model lherzolite or harzburgite in Fo + spinel-saturated liquids.

Decreasing temperature and pressure

Throughout much of this discussion, we have assumed that reactions occur at constant temperature, or at least that solid and liquid reactants are at the same initial temperature. However, in many circumstances, magma rising through the upper mantle may react with wall rock that is colder than the liquid. In these circumstances, the energy demands of heating the solid reactant to magmatic temperatures, and conductive cooling to wall rock not directly in contact with the magma, will serve to cool the liquid and induce crystal fractionation. In a schematic way, the effect of combined assimilation of lherzolite and decreasing temperature can be illustrated using the ternary phase diagrams already presented. In the system Fo–SiO_2–An, for instance, the resulting liquid trend for reaction between Fo + An-saturated liquid and lherzolite might still lie within the Fo field, diagonally leaving the Fo–An cotectic, provided that the ratio of assimilation rate vs. cooling rate (g/°C) was sufficiently large (Fig. 16).

Figure 16 also schematically illustrates the effect of decreasing pressure, which increases the size of the Fo primary phase field. Both reaction with lherzolite and decompression expand the interval of olivine crystallization, for a liquid initially saturated in both olivine and plagioclase. In addition to this, adiabatic decompression will increase the proportion of liquid in natural mafic and ultramafic systems. As a consequence, the Mg/Fe ratio of resultant liquid and solid phases will be greater than in the same system at constant pressure. The combination of wall rock reaction and decompression expands the interval of olivine crystallization more than either process alone, and may produce olivine more magnesian than reactant olivine, even under conditions of constant or decreasing temperature.

APPLICATION TO NATURAL SYSTEMS

In phase diagrams for simple silicate systems, we have seen that isothermal reaction between fractionated basalt and refractory peridotite in wall rock will usually result in an increase in the Mg/Fe ratio of the derivative liquid. Furthermore, it has been shown that reaction between liquid saturated in Fo + An, Fo + Di, and Fo + Mg–Al–spinel with model

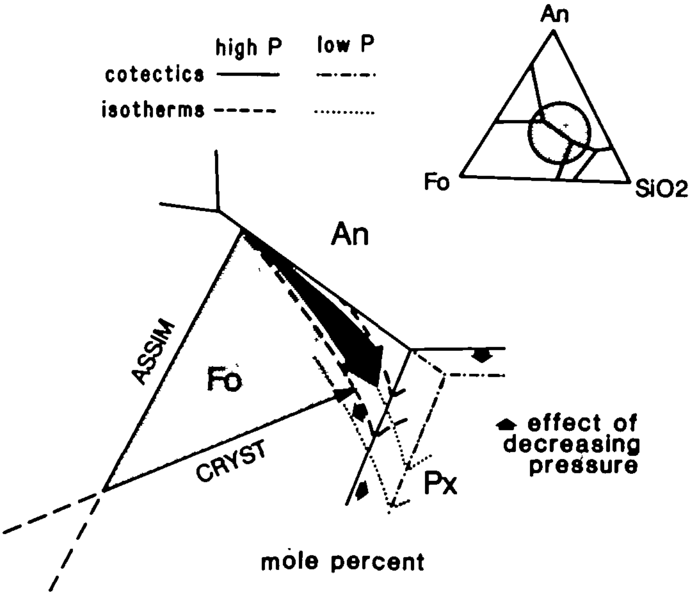

FIG. 16. Schematic illustration of the effects of combined assimilation of lherzolite, decreasing temperature, and decreasing pressure, in a portion of the system Fo–SiO_2–An. Decreasing pressure stabilizes olivine and plagioclase relative to pyroxene, and causes the isothermal liquidus surface in the olivine field to move toward the olivine apex. The liquid trend illustrated corresponds approximately to a 50 °C temperature drop during assimilation of about 1 part (by mass) harzburgite in 1 part liquid. Mantle–magma interaction in such a decompressing system may produce abundant, magnesian dunites from a tholeiitic parent, even under conditions of decreasing temperature. (See text for further discussion.)

lherzolite or harzburgite at constant temperature will produce forsterite and a liquid saturated only in forsterite. It remains to be demonstrated how these relations can be combined and applied to natural solid–liquid reaction in the upper mantle.

Effect of increasing mg*-number on basalt–lherzolite reaction: dunite and wehrlite*

Let us first consider the general effects of increasing MgO/(MgO + total Fe as FeO), i.e., the *mg*-number, in the liquid (and the bulk composition) in an open system. This can be done in a schematic way, by estimating the partitioning of Mg/Fe among the various solid phases. At equilibrium, the phase with the highest Mg/Fe will be stabilized relative to the other phases by an increase in the Mg/Fe ratio of the system. This approach, often used in metamorphic petrology, has recently been illustrated for mafic igneous systems by Longhi (1987). Figure 17 depicts the effect of increasing *mg*-number on the position of cotectic boundaries and isotherms in two of the simple ternary systems already discussed.

In the system olivine–SiO_2–plagioclase (Fig. 17A), increasing *mg*-number will cause both the olivine–plagioclase cotectic and isotherms in the olivine stability field to move away from the olivine apex. It is difficult to predict whether isotherms will move ‘more’ or ‘less’, in composition space, than the cotectic. If isotherms move ‘less’, then the general conclusions developed for the iron-free equivalent system, Fo–SiO_2–An, will hold true in the iron-bearing system, i.e., assimilation of lherzolite will move the liquid off the olivine–plagioclase cotectic into the olivine stability field. If, on the other hand, the isotherms move further than the cotectic, for some increment of reaction progress increasing the *mg*-number of the system, then liquid assimilating lherzolite will remain on the olivine plagioclase cotectic,

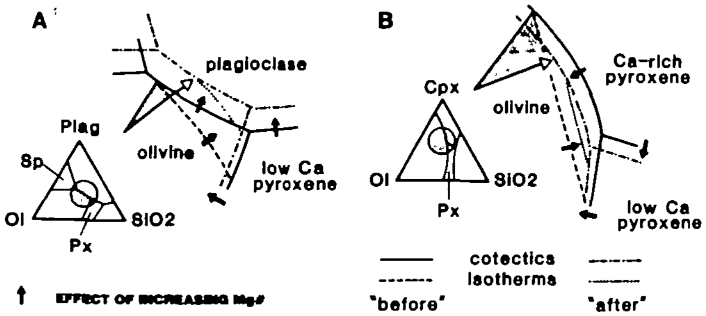

FIG 17. Effect of isothermal assimilation of lherzolite in multiply saturated basaltic liquids in iron-bearing systems, schematically illustrated in olivine–plagioclase-SiO_2 and olivine–calcic pyroxene–SiO_2 pseudo-ternary phase diagrams. In iron-bearing systems, isothermal reaction will tend to increase the *mg*-number weight or mol % *mg*-number [$= MgO/(MgO + \text{total Fe as } FeO)$]. This effect, in turn, will tend to shift the position of cotectic surfaces and isotherms in the pseudo-ternary systems. In olivine–plagioclase–SiO_2, it is predicted that (olivine + plagioclase)-saturated liquids will move off plagioclase saturation with assimilation of lherzolite at constant temperature in a natural system. In olivine–calcic pyroxene–SiO_2, constant-temperature assimilation of lherzolite in olivine–clinopyroxene-saturated liquids will not move the liquid away from clinopyroxene saturation in natural systems, but will produce clinopyroxene-bearing dunite rather than olivine clinopyroxenite with cotectic proportions of olivine and clinopyroxene. (See text for further discussion.)

crystallizing a small amount of plagioclase as well as olivine. Calculations for natural systems, discussed near the end of this section, show that the former possibility is more likely; basaltic liquids, initially saturated in olivine + plagioclase, assimilating lherzolite at constant temperature (or constant enthalpy) will move away from plagioclase saturation.

In the system olivine–SiO_2–calcic pyroxene (Fig. 17B), the effect of increasing *mg*-number is significantly different. The olivine–calcic pyroxene cotectic will shift toward the olivine apex, whereas isotherms within the olivine stability field will move away from the olivine apex. In these circumstances, it is unlikely that a liquid saturated in olivine + calcic pyroxene, assimilating lherzolite at constant temperature, will move off the olivine–calcic pyroxene cotectic, in contrast to the relations shown previously for the iron-free equivalent system, Fo–SiO_2–Di. Calculations for natural systems confirm this conclusion.

However, assimilation of lherzolite in the olivine–SiO_2–clinopyroxene system does produce liquid and crystal products distinctly different from those produced by cotectic crystallization in a closed system. In particular, it is noteworthy that the cotectic proportion of olivine to calcic pyroxene in Fig. 17 is ~1 : 9 (by weight), whereas in the schematic example shown, the proportion of olivine to clinopyroxene crystallized is ~9 : 1. Whereas it is impossible to produce clinopyroxene-bearing dunite or wehrlite by pure fractional crystallization in a closed system, clinopyroxene dunite and/or olivine-rich wehrlite are the natural products of reaction between basalt saturated in calcic pyroxene and peridotite wall rock. Wehrlite in the transition zone in ophiolites, in plutonic rocks intruding alpine peridotite, and in 'Klamath-type' concentrically zoned, calc-alkaline ultramafic to felsic plutonic complexes [for instance, Bear Mountain, described by Snoke *et al.* (1981), and Emigrant Gap, studied by James (1971)], may be formed by reaction of fractionating basalt with high-temperature, ultramafic wall rock, as proposed by Kelemen & Ghiorso (1986).

Decreasing temperature combined with basalt–peridotite reaction: calc-alkaline magma series

Figure 18 illustrates some other general aspects of reaction between basalt and ultramafic wall rock in natural systems using the familiar AFM diagram. Increments of decreasing

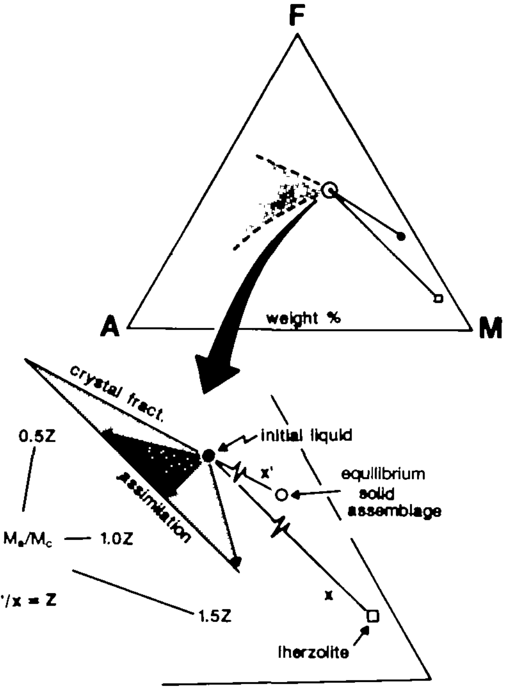

FIG 18. Weight per cent AFM diagram ($A = Na_2O + K_2O$, $F = FeO + 0{\cdot}9Fe_2O_3$, $M = MgO$) and inset illustrating the effect of an infinitesimal amount of crystal fractionation combined with assimilation of peridotite. Solid circle: composition of the initial liquid; open square: composition of the peridotite assimilate; open circle: solid assemblage in equilibrium with the initial liquid. Dashed lines in the full AFM diagram indicate hypothetical evolution of the initial liquid toward tholeiitic and calc-alkaline derivatives. In the inset, vectors show the infinitesimal change in liquid composition as a function of mass lherzolite assimilated/mass crystals produced (M_a/M_c). The lever-rule method used is valid even though the reactants contain different proportions of AFM components. It may readily be seen that, in the case illustrated, crystal fractionation alone will produce iron enrichment (increasing Fe/Mg) in derivative liquids. Derivative liquids produced by combinations of crystallization and assimilation will be less iron enriched (lower Fe/Mg) than those produced in a closed system. At a given Fe/Mg ratio, the liquids resulting from combined crystallization and assimilation will also be more alkaline [have higher alkalis/(alkalis + Fe + Mg)] than those produced in a closed system. Integration of many such-infinitesimal steps, combined with changing composition of the crystal assemblage produced, can produce a calc-alkaline liquid line of descent if crystallization is combined with assimilation of peridotite.

temperature cause iron enrichment in liquids saturated in ferro-magnesian silicates. Assimilation of a magnesian wall rock in the same liquid, at constant or decreasing temperature, results in a less iron-enriched derivative liquid. The exact direction of the incremental liquid line of descent depends on M_a/M_c, as illustrated schematically in the figure. In most cases, the derivative liquid will be more alkaline, as well as less iron enriched, than liquids formed by crystal fractionation alone.

In addition, we have seen previously that liquids saturated in olivine and undersaturated in low-Ca pyroxene (partial melts of four-phase peridotite at pressures less than the pressure of melting), reacting with lherzolite or harzburgite, will dissolve low-Ca pyroxene from the wall rock, and crystallize a smaller mass of olivine as a consequence. This kind of reaction should lead to silica enrichment in derivative liquids in natural as well as simple systems. Kelemen (1986) has already shown that liquids produced from initially tholeiitic magmas assimilating magnesian olivine (Fo_{90}) are more silica rich, less iron enriched, and more alkaline than liquids produced from tholeiitic magmas by crystal fractionation without assimilation, as Fe–Mg exchange reactions between magnesian olivine and liquid fractionate fayalite component from the melt. In short, mantle–magma interaction involving olivine-saturated liquid should generally produce calc-alkaline derivative liquids.

Although this is a compelling theory, we might discard it if the derivative liquids so produced were a much smaller fraction of the parental liquid mass than derivative liquids resulting from crystal fractionation alone. As discussed above, likely Fe–Mg exchange reactions cause a slight decrease in the total liquid mass in the system ($M_a/M_c < 1$), whereas pyroxene dissolution from lherzolite leads to a small increase in the total liquid mass ($M_a/M_c > 1$). At constant temperature, Fe–Mg exchange reactions are slightly exothermic whereas most plausible lherzolite assimilation reactions are slightly endothermic, at least in simple systems. Calculations of the effect of isenthalpic reaction between basalt and lherzolite in natural systems, presented at the end of this paper, indicate that the slight exothermic effect of 'Fe–Mg exchange' and the slight endothermic effect of pyroxene dissolution are approximately balanced, producing a phase assemblage with a nearly constant mass of liquid, and causing little change in temperature. As a first approximation, such reactions are naturally isenthalpic at constant temperature, and M_a/M_c is nearly equal to one. Results of experiments on basalt–harzburgite mixtures, presented by Kelemen *et al.* (1987, 1990), fully support these conclusions.

Two-dimensional projections which can be used to illustrate processes in multi-component igneous systems have been developed by Walker *et al.* (1979), Grove *et al.* (1982), and Elthon (1983). The most frequently used versions are projections of the plagioclase-saturated cotectic surfaces onto the plane olivine–silica–calcic pyroxene, analogues for a projection from An onto the Fo–SiO_2–Di plane. In recent years, Grove and others (Grove & Baker, 1984; Grove & Kinzler, 1986) have stressed the point that calc-alkaline volcanic rock compositions, plotted on such diagrams, form trends distinct from those formed by tholeiitic volcanic rock compositions. Grove and others restricted discussion to suites in which the most primitive melt compositions in both calc-alkaline and tholeiitic series are similar. Thus both series may have broadly similar parental melts.

Only tholeiitic series and the more iron-enriched calc-alkaline series follow the 'high-pressure' cotectics plotted by Grove & Baker (1984) and Grove & Kinzler (1986). Liquid trends which lie well within the calc-alkaline field of Irvine & Baragar (1971), for instance, the Lesser Antilles 'series' and the Aleutian series, follow trends which are oblique to any experimentally determined cotectics, high or low pressure, wet or dry, but remain stubbornly within the olivine primary phase volume on Grove's projection until they reach very fractionated (i.e., silicic) compositions. In effect, these series follow a trend from the 10-kb olivine–two pyroxene–spinel pseudo-invariant 'point' directly towards the silica apex. These data are presented in Fig. 19.

Figure 19D illustrates the probable effects of basalt–mantle interaction on the liquid line of descent. As in the Fo–Di–SiO_2 phase diagram, potential lherzolite and harzburgite assimilates lie in the olivine field near the olivine–SiO_2 join. High-pressure partial melts of peridotite in natural systems lie in the olivine field, near the olivine–calcic pyroxene join, as do high-alumina basalts considered primary melts from oceanic crust in subduction zones by Myers and co-workers (Myers *et al.*, 1985; Myers & Marsh, 1987; Myers, 1988). It is clear from this diagram that assimilation of mantle peridotite, coupled with fractionation of olivine under conditions of slowly decreasing temperature and pressure, with or without crystallization of plagioclase, spinel, clinopyroxene, or hornblende, could produce calc-alkaline trends like those illustrated in Fig. 19A–C.

Figure 19D is topologically almost identical to fig. 5 of Grove *et al.* (1982) and fig. 12 of Grove & Baker (1984), but these authors showed that the trend of the Medicine Lake

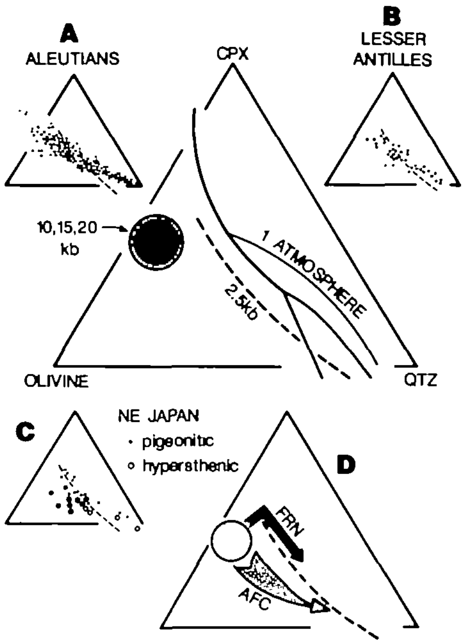

FIG. 19. Projections from plagioclase onto the olivine–clinopyroxene–silica base of the pseudo-quaternary system olivine–clinopyroxene–silica–plagioclase, constructed using the method of Grove *et al.* (1982). Central triangle shows the 1 atm cotectics of Grove *et al.* (1982), based primarily on experimental data for dry mid-ocean ridge compositions, as solid lines. The shaded circle encloses the compositions of basaltic liquids in equilibrium with mantle peridotite at 8–20 kb. Data from Kushiro *et al.* (1972), Kushiro (1972*a*, 1973), Thompson (1974, 1975), Elthon & Scarfe (1980, 1984), Stolper (1980), Takahashi & Kushiro (1983), and Fujii & Scarfe (1985) much of it compiled by Grove & Kinzler (1986). The 2·5 kb, H_2O-undersaturated olivine–calcic pyroxene cotectic of Spulber & Rutherford (1983) is shown as a dashed line, and retained for reference in all the smaller diagrams. (A) Aleutian data from Kay *et al.* (1982), Baker & Eggler (1983, 1987), Kay & Kay (1985), and Baker (1987). (B) Lesser Antilles data compiled by Grove & Kinzler (1986) from Sigurdsson *et al.* (1973), Arculus (1976), Brown *et al.* (1977), and Dostal *et al.* (1983). Only silica-saturated compositions are plotted. (C) Data on pigeonitic and hypersthenic series of Japan from Kuno (1950, 1960, 1968), compiled by Grove & Kinzler (1986). (D) Schematic illustration of the effect of crystal fractionation in a closed system (FRN), and combined assimilation of mantle wall rock and crystal fractionation (AFC), on a parental melt which was initially in equilibrium with lherzolite at high pressure. Both processes are assumed to have taken place at moderate pressure under the same conditions of temperature and initial liquid composition. Figure 19D is topologically almost identical to Fig. 5 of Grove *et al.* (1982) and Fig. 12 of Grove & Baker (1984), but these authors showed that the trend of the Medicine Lake volcanic series was due to crustal assimilation. The effects of interaction between wall rock and fractionating basalt are broadly similar on this projection. (See text and caption to Fig. 20 for further discussion.)

volcanic series was due to crustal assimilation. Indeed, the effects of combined assimilation and fractional crystallization (AFC) are broadly similar for reaction with mantle or crustal wall rock on the projection of Grove *et al.* (1982). However, the effects of crustal vs. mantle AFC are quite distinct on an AFM diagram (Fig. 20). To 'buffer' the Fe/Mg ratio in derivative liquids at low values, the assimilate must lie below the trend formed by calc-alkaline liquid series on an AFM diagram. Assimilation of mafic crustal rock (amphibolites, mafic granulites) and/or assimilation of highly evolved silicic melts at superliquidus temperatures might be candidates in individual cases, but equilibrium assimilation of typical crustal metasediments cannot account for the difference between calc-alkaline and tholeiitic liquid lines of descent (Kelemen, 1988).

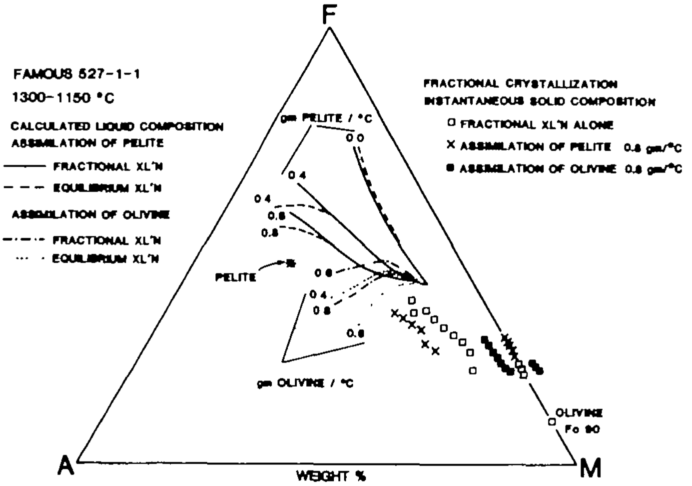

FIG. 20. Weight per cent AFM diagram, as for Fig. 18, comparing calculated liquid lines of descent for (a) closed-system crystallization (curve labelled 0-0), (b) combined assimilation of pelitic wall rock and crystallization, and (c) combined assimilation of magnesian olivine (Fo_{90}) and crystallization. Curves are labelled in terms of grams assimilated per °C temperature drop. Solid and liquid compositions predicted using the solution model of Ghiorso and others (Ghiorso *et al.*, 1983; Ghiorso, 1985; Ghiorso & Carmichael, 1985; Ghiorso & Kelemen, 1987) implemented as the computer program SILMIN. Input parameters are the initial liquid composition, the composition of the assimilate, temperature, pressure, oxygen fugacity, and rate of assimilation in g assimilated/°C temperature drop. Initial liquid composition was the same in all cases, that of the magnesian MORB, FAMOUS 527-1-1 (studied experimentally by Bender *et al.*, 1978). The pelitic rock composition was constructed using a weighted average of group analyses of shale and slate compiled by Clarke (1924), with volatiles removed. The bulk composition and mineral assemblage used are given in Tables 1 and 2.

Calculations using a solution model (SILMIN) for natural silicate liquids and coexisting solid phases

This section presents results from calculations of equilibrium assemblages formed during assimilation of perioditite in basalt. These calculations, for natural silicate liquid and solid compositions; were made using the computer program SILMIN, the implementation of an expanded regular solution model for natural silicate liquids, developed and described by Ghiorso and others (Ghiorso *et al.*, 1983; Ghiorso, 1985; Ghiorso & Carmichael, 1985; Ghiorso & Kelemen, 1987). Two kinds of calculation will be presented: (1) calculation of the effect of isenthalpic reaction between saturated basalt and peridotite, in which reactants are at the same initial temperature, and (2) calculation of the effect of combined cooling and assimilation of peridotite in crystallizing basaltic liquids. The first type of calculation may approximately model the process of mantle–magma interaction when wall rock and magma are at similar temperatures, as there will be little driving force for heat conduction in or out of the reacting system. The second type of calculation is designed to model reaction of basalt with wall rock which is well below the initial temperature of the liquid. Although isenthalpic assimilation under these conditions certainly produces a decrease in temperature, in natural systems loss of heat to cold wall rock also serves to cool the magma. Thus the relative rate of assimilation vs. cooling (in grams assimilated/°C) used in these calculations is greater than that which would be predicted for an isenthalpic system.

In addition to the magnesian MORB (FAMOUS 527-1-1) used in calculations presented in Fig. 20, three initial liquid compositions were used in these calculations: (1) a picrite (NT23) from the Tortuga ophiolite studied experimentally by Elthon & Scarfe (1984); (2) a magnesian island-arc tholeiite (MK15) from Makushin volcano on Unalaska Island in the Aleutian chain, studied experimentally by Gust & Perfit (1987); and a composite high-Fe/Mg, high-alumina basalt composition selected by Myers (1988) to be representative of possible liquids derived by partial melting of oceanic crust in a subduction zone. Compositions of these liquids are given in Table 1. They were chosen because fractionation of olivine from picritic liquids is a proposed explanation for the formation of discordant dunite (e.g., Quick, 1981*b*), and the other two compositions have been suggested to be near primary, parental liquids for both tholeiitic and calc-alkaline magma series in the Aleutian arc. Given that the goal was to investigate reaction between basaltic liquids and peridotite, the compositions chosen could hardly be more diverse. Two compositions, a lherzolite and a harzburgite, were used for the solid assimilate (Table 2). The lherzolite contained 70 wt. % olivine (Fo_{89}), 20 wt.% orthopyroxene (En_{90}), 8 wt.% calcic pyroxene ($Wo_{47}En_{51}Fs_{02}$), and 2 wt. % plagioclase (An_{90}). The harzburgite used had 70 wt. % olivine (Fo_{89}) and 30 wt. % orthopyroxene (En_{90}). Despite this variety in solid and liquid reactants, the results of the calculations for the different bulk compositions are so similar that they can all be discussed together. The isenthalpic models will be treated first, and then the predicted results of assimilation under conditions of falling temperature will be described.

All calculations were performed at 3 kb on the FMQ oxygen buffer, in systems without H_2O. In this, and all other modelling using SILMIN, all phase proportions and compositions are calculated. In addition, temperature is calculated in isenthalpic runs. Although it is recognized that 3 kb is a low pressure for natural magma–mantle interaction, the present version of the solution model is not accurate at higher pressure. It may be argued that silica enrichment produced by reaction between crystallizing magma and peridotite is entirely an artefact of the low pressures used in modelling. However, this is not the case. As shown by Presnall *et al.* (1979), the plane En–Di–An in the system Fo–Di–An–SiO_2, and its analogue in natural systems, is not a 'thermal barrier' at elevated pressure, and does not prevent silica enrichment in liquids derived from olivine normative parents, even at 20 kb. At pressures >3 kb in 'dry' systems, pyroxenes would be more stable relative to olivine, and their crystallization might suppress silica enrichment in individual cases. However, addition of small amounts of H_2O to the systems modelled would have the opposite effect, stabilizing olivine relative to pyroxene at a given pressure, and enhancing silica enrichment due to reaction.

TABLE 1

Liquid compositions used in modelling, weight per cent oxides

	*FAMOUS 527-1-1**	*MK†*	*MHAB‡*	*NT23§*
SiO_2	48·65	50·98	49·50	47·90
TiO_2	0·74	0·75	0·95	0·85
Al_2O_3	16·45	15·62	19·50	13·47
FeO‖	8·99	9·18	9·50	9·62
MgO	10·80	9·60	4·50	16·95
CaO	12·11	10·08	10·50	9·98
Na_2O	1·97	2·76	3·10	1·07
K_2O	0·09	0·92	0·75	0·05

* FAMOUS 527-1-1 from Bender *et al.* (1978).

† MK15 from Gust & Perfit (1987).

‡ MHAB from Myers (1988).

§ NT23 from Elthon & Scarfe (1984).

‖ All Fe as FeO. In modelling, ferric/ferrous ratio in the liquid was calculated for the FMQ oxygen buffer using the method of Kilinc *et al.* (1983).

TABLE 2

Solid compositions used in modelling, weight per cent mineral end-members

		*Pelite**	*Harzburgite*	*Lherzolite*
Olivine	Forsterite		59·40	59·40
	Fayalite		10·60	10·60
Opx	Enstatite	4·80	26·18	17·45
	Ferrosilite	7·33	3·82	2·55
Cpx	Enstatite			0·48
	Ferrosilite			0·43
	Diopside			7·09
Plagioclase	Anorthite	15·40		1·81
	Albite	13·48		0·19
Sanidine		21·02		
β-Quartz		28·72		
Ilmenite		1·39		
Spinel	Hercynite	4·94		
	Spinel	2·93		

* Pelitic composition obtained by averaging the group analyses for shale and slate reported by Clarke (1924, pp. 552 and 631). H_2O, CO_2, SO_2, C, P_2O_5, and trace components in the analyses were ignored; other oxides normalized to 100 wt. %, and recast in terms of mineral end-members for use with the silicate liquid solution model. Spinel and quartz, rather than sillimanite and quartz, were used for convenience of calculation.

Isenthalpic assimilation calculations

Only the arc tholeiite (MK15) and the high-alumina basalt (MHAB) compositions were used in these calculations. Each was at an initial temperature of 1260 °C, at 3 kb. At this temperature, MK15 is predicted to be 20 °C below its liquidus, saturated only in olivine, in agreement with the experimental results of Gust & Perfit (1987). MHAB is predicted to be just saturated in plagioclase (An_{74}), as would be expected from the experimental results of Baker & Eggler (1983, 1987) and Johnston (1986) for other high-alumina basalts. In both liquids, isenthalpic assimilation of peridotite (solid assimilate at 1150 °C) results in a calculated 15–20 °C temperature drop, followed by reaction which maintains the system at nearly constant temperature. Throughout the calculations (assimilation of 400 g peridotite in 100 g initial liquid) the mass of liquid, the SiO_2 concentration in the liquid, and the liquid *mg*-number all increase. These and other results are presented in Fig. 21 and Table 3. It should be noted that the increase in silica concentration in derivative liquid continues even after saturation in both clino- and orthopyroxene.

Particularly important are the predicted solid-phase proportions and compositions. Despite the disparate *mg*-numbers of the initial liquids, olivine compositions produced by reaction with peridotite are amazingly similar, and fall in the restricted range Fo_{83-89}. Furthermore, the solid-phase compositions in both systems correspond to the composition of dunite and clinopyroxene dunite for the first 200 g peridotite added to 100 g initial liquid. This is so even though MHAB is initially saturated in plagioclase. In MHAB, over the first 5 g lherzolite assimilated, olivine (Fo_{83}) appears on the liquidus. After 15 g have been assimilated, plagioclase crystallization ceases, despite the fact that the lherzolite contains 2 wt. % plagioclase. Clearly, assimilation of high-temperature peridotite wall rock in tholeiitic basalt is a process which can produce voluminous, homogeneous, magnesian dunites, even when the initial liquid is saturated in plagioclase and has high Fe/Mg and low MgO concentration. By no means could derivative liquids be described as picritic; on the

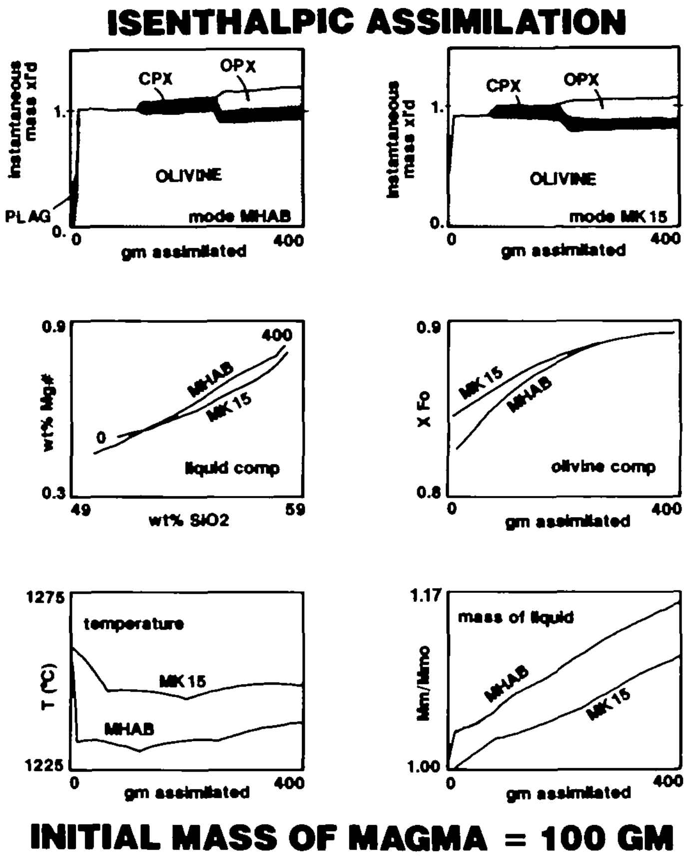

FIG 21. Results of calculations modelling isenthalpic assimilation of peridotite in a magnesian island-arc tholeiite (MK15, Gust & Perfit, 1987) and a high-Fe/Mg, high-alumina basalt (primary, parental Aleutian basalt of Myers, 1988: 'MHAB') using the computer program SILMIN, a solution model for natural silicate liquids developed by Ghiorso and others (Ghiorso *et al.*, 1983; Ghiorso, 1985; Ghiorso & Carmichael, 1985; Ghiorso & Kelemen, 1987). Instantaneous mass xl'd = 100(instantaneous mass crystallized/mass of liquid); wt. % *mg*-number = wt. % MgO/(MgO + FeO^{total}); *X* Fo = mole fraction forsterite in olivine; M_m/M_{m_0} = mass of magma/initial mass of magma. Tables 1 and 2 give the initial compositions of liquid and solid reactants. Table 3 gives complete compositions for predicted liquids derived from MHAB ± lherzolite. Phase compositions, phase proportions, and temperatures are all calculated given initial temperature (1260 °C), pressure (3 kb), bulk composition of the liquid, mass assimilated, bulk and phase composition of the assimilate (harzburgite in MK15, lherzolite in MHAB), and oxygen fugacity (FMQ). Predicted increase in liquid mass is due to the high enthalpy of fusion used for forsterite; please see note added in proof, (p. 93).

contrary, they are enriched in silica relative to the parental liquid composition, approaching the composition of boninites. Although these calculations are for interaction at constant pressure, the production of dunite, and its effect on derivative liquid, would be extended in a system undergoing decompression.

Assimilation in conditions of decreasing temperature

As with isenthalpic assimilation, results for modelling of assimilation of peridotite in fractionating basalt under imposed conditions of decreasing temperature in several disparate initial liquid compositions are amazingly similar, and can all be described together. Results of modelling assimilation of harzburgite in arc tholeiite (MK15) and picrite (NT23) and for assimilation of lherzolite in high-Fe/Mg, high-alumina basalt (MHAB) are shown in

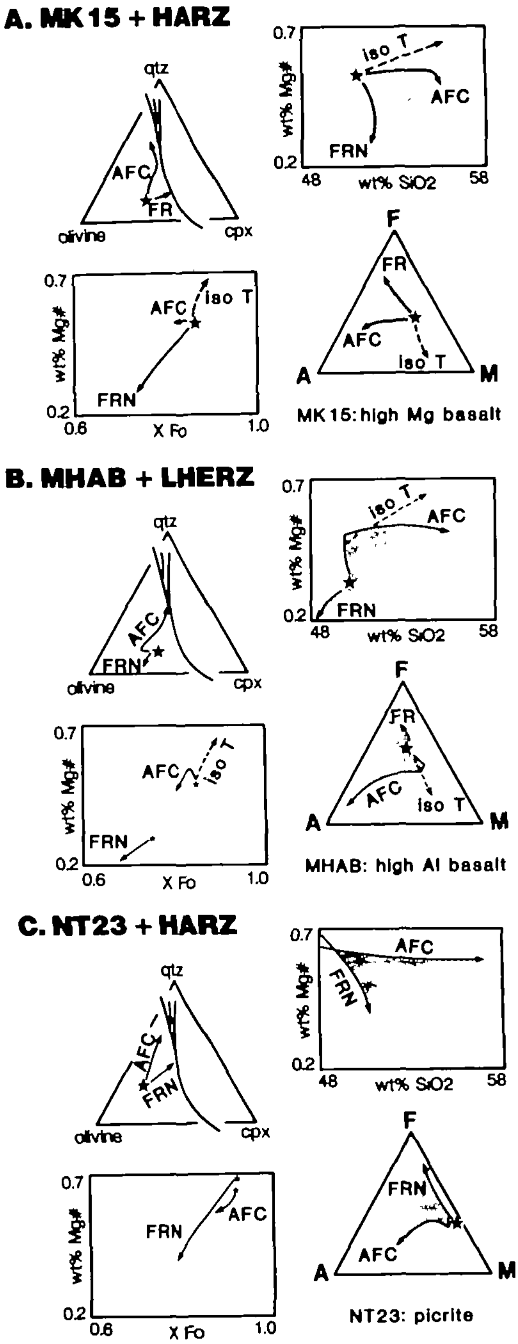

FIG 22. Results of calculations modelling assimilation of peridotite in a magnesian island-arc tholeiite (MK15), a high-Fe/Mg, high-alumina basalt (MHAB), and a picritic liquid (NT23, from Elthon & Scarfe, 1984), under externally imposed conditions of falling temperature, using the computer program SILMIN, a solution model for natural silicate liquids developed by Ghiorso and others. Tables 1 and 2 give the initial compositions of solid and liquid reactants. Table 3 gives complete chemical compositions for several predicted liquids. Results for assimilation with falling temperature (AFC) are contrasted with the trend for isothermal assimilation of harzburgite (iso T), and the trend for fractional crystallization without assimilation (FRN). Olivine–cpx–qtz diagrams are projections from plagioclase in the pseudo-quaternary system olivine–calcic pyroxene–plagioclase–silica ('quartz'), constructed

Fig. 22 and Table 3. For comparison, trends for fractional crystallization in a closed system, and for isothermal assimilation of 100 g of peridotite in 100 g of initial liquid, are also presented in these diagrams.

In all three cases, the liquid line of descent for assimilation with falling temperature is calc-alkaline on an AFM diagram and oblique to experimentally determined olivine–pyroxene–plagioclase cotectics on the projection of Grove *et al.* (1982). The liquid trends produced by fractional crystallization show strong iron enrichment on the AFM diagram and (with the exception of MHAB) evolve along cotectics in the Grove projection. Combined assimilation and decreasing temperature produces increasing concentration of SiO_2 at nearly constant *mg*-number in derivative liquids, whereas liquids produced by fractional crystallization show constant or decreasing SiO_2 concentration and decreasing *mg*-number under the same conditions of temperature, pressure, and initial bulk composition. It should be noted that constant *mg*-number in the assimilation cases is accompanied by decreasing concentration of both FeO and MgO in derivative liquids. Finally, olivine compositions are consistently magnesian in the assimilation models, and parallel the liquid trend of iron enrichment in the fractional crystallization cases.

All three liquids have extended intervals of olivine fractionation in the assimilation models. With assimilation of peridotite, olivine is alone on the liquidus for $>50\,^{\circ}C$ in MK15 and MHAB, or $\sim 25\%$ of the equilibrium crystallization interval for these liquids at 3 kb. This is striking in the case of MHAB, whose closed-system crystallization sequence is plagioclase at 1260 °C, followed by clinopyroxene at 1220 °C, and olivine at slightly less than 1200 °C. In the picrite, of course, the olivine crystallization interval spans more than 100 °C regardless of whether peridotite is added or not, but the range in predicted olivine composition is much larger in the closed-system calculation.

In the case of the high-alumina basalt (MHAB), all these phenomena would be less striking if the calculation were begun at 1260 °C, where the liquid is predicted to become saturated in plagioclase, rather than at 1300 °C, 40° above its liquidus. Myers (1988) has suggested that MHAB could be a primary melt from oceanic crust in the downgoing slab in a subduction zone. Under geologically reasonable conditions, ascending melts might (temporarily) be superliquidus if a portion of the ascent path traverses wall rock at temperatures greater than that of the liquid.

Below ~ 1200–1180 °C, all modelled liquids are predicted to become saturated in orthopyroxene. Olivine disappears from the liquidus at slightly lower temperatures. Despite this change, silica enrichment continues in liquids derived by combined crystal fractionation and reaction with peridotite. This is true because, by the time these systems reach 1200 °C, the liquids contain >54 wt.% SiO_2, which is greater than the concentration of silica in predicted, cotectic proportions of orthopyroxene, clinopyroxene, and plagioclase. In the closed system crystallization of MK15 and MHAB, SiO_2 concentration decreases in

Fig. *caption* continued from *p.* 38

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using the method of Grove *et al.* (1982). One-bar cotectics defined by Grove *et al.* are shown for reference. Wt. % *mg*-number = wt. % $MgO/(MgO + FeO^{total})$. It should be noted that *mg*-number can be constant or increasing even when MgO content of the liquid is decreasing. X Fo = mole fraction forsterite component in olivine. AFM diagram in weight per cent; $A = Na_2O + K_2O$, $F = FeO + 0{\cdot}9Fe_2O_3$, $M = MgO$. Phase compositions, phase proportions, and temperatures are all calculated given initial and final temperature (1300–1150 °C for MK15 and MHAB, 1460–1150 °C for NT23), pressure (3 kb), bulk composition of the liquid, oxygen buffer (FMQ), bulk and phase composition of the assimilate (harzburgite or lherzolite: see text), and rate of assimilation in g/°C/100 g liquid in the system (0·67 for MK15 and MHAB, 2·0 for NT23). In the calculations presented here, this rate was held constant, whereas in the past (Kelemen, 1986; Kelemen & Ghiorso, 1986; Ghiorso & Kelemen, 1987; Fig. 20, above) calculations were made at constant ratio of grams assimilated/°C, regardless of the mass of liquid remaining in the system.

TABLE 3

Calculated liquid compositions (oxides in weight per cent) produced by modelling combined assimilation of peridotite and fractional crystallization of basaltic liquid, using a solution model for natural silicate liquids (SILMIN: Ghiorso et al., *1983; Ghiorso, 1985; Ghiorso & Carmichael, 1985; Ghiorso & Kelemen, 1987); initial liquid and peridotite compositions are given in Tables 1 and 2*

	Combined falling temperature and assimilation							*Isenthalpic assimilation*		
Liquid	*MHAB**	*MHAB*	*MHAB*	*MK15**	*MK15*	*NT23**	*NT23*	*MHAB**	*MHAB*	*MHAB*
Assimilate	*none**	*lherz*	*lherz*	*none**	*harz*	*none**	*harz*	*none**	*lherz*	*lherz*
Initial temp. (°C)	*1300**	*1300*	*1300*	*1300**	*1300*	*1460**	*1460*	*1260**	*1260*	*1260*
Final temp. (°C)	*1200**	*1270*	*1200*	*1200**	*1200*	*1250**	*1250*	*1230**	*1231*	*1238*
Rate of assim.†	*0**	*0·67*	*0·67*	*0**	*0·67*	*0**	*2·00*	*0**	*100 g*	*400 g*
SiO_2	50·02*	49·97	53·94	51·91*	55·11	49·66*	56·10	50·27*	54·03	58·09
TiO_2	1·38*	0·84	1·83	1·18*	1·64	1·06*	0·99	1·18*	0·87	0·82
Al_2O_3	14·83*	17·46	19·56	15·92*	17·61	16·76*	15·64	17·17*	17·42	17·04
Fe_2O_3	2·16*	1·28	0·96	1·66*	0·95	1·23*	0·68	1·79*	0·71	0·25
FeO	11·84*	8·12	5·54	9·30*	5·47	8·27*	4·90	10·16*	4·46	1·34
MgO	6·53*	9·15	5·20	6·58*	5·34	9·20*	8·81	5·58*	7·87	6·65
CaO	9·21*	9·74	7·97	8·78*	8·30	12·41*	11·58	9·82*	11·21	12·58
Na_2O	3·01*	2·76	3·65	3·28*	3·66	1·34*	1·25	3·13*	2·76	2·62
K_2O	1·03*	0·67	1·39	1·39*	1·91	0·06*	0·06	0·90*	0·68	0·64
mg-number	0·32*	0·50	0·45	0·38*	0·46	0·49*	0·62	0·32*	0·61	0·81
M_m/M_{m_o}‡	0·69*	1·13	0·52	0·63*	0·46	0·80*	0·86	0·80*	1·10	1·16

* Fractional crystallization without assimilation. Results given for comparison with assimilation calculations.

† Rate of assimilation for combined falling temperature and assimilation calculations in g assimilated/°C/100 g liquid in the system. Total grams of peridotite assimilated are given for the isenthalpic assimilation calculations.

‡ M_m/M_{m_o} = mass of magma/initial mass of magma.

predicted liquid compositions after orthopyroxene replaces olivine on the liquidus, because the liquids contain $\sim$50 wt.% SiO_2, which is less than the concentration of SiO_2 in the crystallizing assemblage.

In Fig. 22, the liquid trends are shown all the way to an extreme level of fractionation. At 1150 °C, some of these dry systems are predicted to be >80% crystallized. [In the AFC cases, 'per cent crystallized' is calculated as $100\% \cdot (1 - \text{mass of magma/initial mass of magma})$.] In these circumstances, liquid compositions predicted by SILMIN are rather unrealistic in many ways. For example, in the present version of the solution model, titanium is a perfectly incompatible element, and thus there is a fivefold titanium enrichment in derivative liquids when 80% of the initial liquid has crystallized. In addition, it is unlikely that significant quantities of calc-alkaline liquids as evolved as dacite are produced directly by mantle–magma interaction.

Table 3 illustrates predicted liquid compositions at temperatures of 1200 °C and above, where the modelled systems are <55% crystallized. In all the cases involving combined crystallization and reaction with peridotite, the liquids produced at this stage are calc-alkaline andesites, whereas the liquids produced by closed-system crystallization are tholeiitic basalts, by the definitions of Irvine & Baragar (1971) and Gill (1981). It is proposed that voluminous calc-alkaline basaltic andesites and andesites are generated from magnesian, tholeiitic parents by mantle–magma interaction under conditions of decreasing magmatic temperature, or by similar interaction between fractionating basalt and mafic to ultramafic cumulates near the crust–mantle boundary. These andesites may then evolve by crystal fractionation, with or without continued wall rock reaction, to more felsic, calc-alkaline derivatives.

DISCUSSION

It is clear from the results of modelling that combined crystallization and assimilation of mantle in cooling basaltic liquids can produce a calc-alkaline liquid line of descent under conditions of temperature, pressure, and initial liquid composition which produce a tholeiitic liquid trend in a closed system. In addition, this process can produce voluminous, compositionally homogeneous dunites with olivine compositions only slightly more iron-rich than those in mantle wall rock.

Discordant dunite

One feature of discordant dunite which has been particularly difficult to explain is its homogeneity. Even extensive dunite bodies show little evidence that they were produced by fractionation (or as restites) from a liquid whose composition was varying. Faced with some of the more extensive dunite bodies, it has been difficult for many petrologists to imagine the immense mass of 'picritic' magma which could precipitate so much magnesian olivine without appreciable evidence of iron enrichment or other expected effects of olivine fractionation. It also seems unlikely that large volumes of magma could pass through centimeter-wide dunite 'dikes', yet they too are composed of homogeneous, Mg-rich olivine.

The process of reaction between a relatively low-temperature, basaltic liquid and refractory lherzolite, occurring at constant temperature and pressure, could form an isobarically, isothermally (pseudo-) invariant liquid composition which was saturated only in magnesian olivine (±chromite). If this process were extensive in time and space, and if the liquid products eventually escaped without extensive cooling *in situ*, it would create large discordant dunite bodies in which the olivine was only slightly more iron-rich than olivine in the wall rock. It is unlikely that such a solid–liquid assemblage could be truly invariant in a natural system; the liquid would eventually 'escape' along some compositional vector corresponding to the remaining degree(s) of freedom. However, the trend of liquid variation, driven by this process, could not be determined from the Fe/Mg ratio of the monotonous dunite 'cumulates' produced, as the *mg*-number of the liquid would be partially buffered by Fe–Mg exchange with minerals in the wall rock. This process does not require crystal fractionation from picritic magmas, but instead extends the interval of olivine fractionation from typical tholeiitic magmas. Olivine-saturated liquids formed in this way would not be 'picritic'; in fact, they would commonly have a higher concentration of silica than the uncontaminated parent magma before reaction.

Calc-alkaline magma series

Much of this paper has concentrated on reaction between mantle-derived, olivine tholeiite magma and mantle wall rock. Partial melting of mantle peridotite, perhaps with the addition of small amounts of fluid derived from the downgoing slab, remains a preferred model for the genesis of magnesian tholeiites in subduction-related magmatic arcs. However, Myers (1988) has suggested that iron-rich high-alumina basalts in the Aleutians are primary melts from the downgoing oceanic slab, and that high-MgO (9 wt.%) magmas in the arc could be formed by interaction between high-alumina basalt and mantle peridotite. This hypothesis is thermodynamically viable, as shown by modelling presented in the section on 'Assimilation in conditions of decreasing temperature' above.

If the downgoing slab in subduction zones does undergo substantial melting, the liquid (or solid–liquid 'mush') produced must rise into hotter mantle material in the overthrust plate. In a closed system, the effect of increasing temperature and decreasing pressure would be to raise this material above its liquidus. However, in an open system, magma above its liquidus will dissolve hotter wall rock until it is saturated in the phases in the wall rock. Liquids derived from anatexis in the downgoing slab, ascending through the mantle wedge, could assume the major-element characteristics of mantle partial melts, as do basaltic liquids in peridotite 'sandwich' experiments. The mass of liquid derived in this manner would be slightly greater than the initial mass of melt produced in the slab, yet it could have the composition of liquid produced by very small degrees of melting of peridotite. Subsequent mantle–magma interaction would be fundamentally similar to interaction between true partial melts of peridotite and mantle wall rock.

The geometry and rheology of melt production and ascent in subduction-related magmatic arcs is poorly understood, and speculation about the details of such processes is bound to be unconstrained. However, whether magmas pass upward through pristine mantle, or conduits filled with ultramafic cumulates, their composition will be affected by reaction with high-temperature wall rocks. It has been proposed by many authors (e.g., Gill, 1981; Conrad & Kay, 1984) that large magma reservoirs may form along the crust–mantle boundary in subduction-related magmatic arcs. This would occur where the density of mafic magma was no longer sufficiently different from the density of wall rock to drive rapid ascent. Melts which become relatively 'felsic' would escape from such reservoirs, leaving behind a consistently mafic, or ultramafic, residuum. In these circumstances, a sequence of hot ultramafic or mafic cumulates with relatively constant composition might form a sort of steady-state 'filter' for ascending magma, partially buffering the *mg*-number, and increasing the silica content, of any melt passing higher in the magmatic arc.

Unlike other proposed explanations for the calc-alkaline trend, interaction of fractionating basalt with high-temperature ultramafic and mafic rock is appealing because it must apply, to some degree, to every magma which passes slowly through the upper mantle and lower crust. Although it is true that every calc-alkaline magma series has specific features which make it unique, and which require the operation of unique processes, this does not mean that there can be no unifying factor in the genesis of all calc-alkaline rocks. Interaction between fractionating basalt and ultramafic to mafic wall rock could be such a unifying factor. Whereas tholeiitic magma series typically develop at divergent plate margins, where wall rock interaction at moderate pressure must be at a minimum, calc-alkaline series occur at convergent margins, and melts pass through almost 100 km of overlying rock to reach the surface. It makes a great deal of intuitive sense that such melts would undergo substantially more interaction with high-temperature wall rock than their tholeiitic cousins. Though much of this interaction might occur in the upper mantle, reaction between more evolved liquids and mafic lower crustal wall rock would have a broadly similar, complementary effect, 'buffering' evolving liquids to relatively high Mg/(Mg+Fe).

Crustal evolution

This process has important implications for Phanerozoic crustal evolution. It is proposed that ascending liquids in magmatic arcs shed much of their iron content in reaction with wall rock in the upper mantle and lower crust, and that the same reaction process removes a significant proportion of silica and alumina from the upper mantle. The net result is that the evolving crust in magmatic arcs is enriched in SiO_2 and Al_2O_3, and depleted in iron, relative to liquids produced by partial melting in the mantle. Furthermore, the sub-arc mantle would have a higher average Fe/Mg ratio, and a higher proportion of olivine, than sub-oceanic mantle. It is probable that inter-oceanic magmatic arcs have basement similar to alpine peridotite, in which sub-oceanic mantle has been modified by interaction with slowly ascending basaltic liquids at nearly constant temperature. Discordant dunite bodies in alpine peridotite may record extraction of sialic crust from the Earth's interior.

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Note added in proof

Navrotsky *et al.* (1989) have published a new estimate for the heat of fusion of forsterite at its melting temperature, about 195 cal/g at 2163 K, which is much lower than the value estimated by Ghiorso & Carmichael (1980), and used throughout this paper, which is 290 cal/g at 2163 K. Use of the lower value for the enthalpy of fusion of forsterite, combined with older data for liquid heat capacities, and for the (estimated) enthalpy of fusion of (clino) enstatite would lead to significant quantitative changes in the results presented here. Specifically, the reaction En + liquid = forsterite would be endothermic for any $M_a/M_c > 1$ at typical basaltic temperatures. Conversely, reactions such as Fo_{90} + liquid = Fo_{80} would be more strongly exothermic. 'Isenthalpic' contours in Figs. 2 and 8 would both be shifted to the left. None the less, qualitative conclusions presented here would be essentially unchanged: isothermal reaction between basalt and mantle peridotite involves very small changes in enthalpy, and isenthalpic reaction would produce nearly constant + Magma mass.

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