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An evaluation of major element heterogeneity in the mantle sources of basalts

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Understanding the evolution of the mantle requires a knowledge of the relative variations of the major elements, trace elements and isotopes in the mantle. Most of the evidence for mantle heterogeneity is based on variations in the trace element and isotopic ratios of basaltic rocks. These ratios are presumed to reflect variations in the mantle sources. To compare major element heterogeneities with trace element and isotopic heterogeneities, it is necessary that the major element abundances in basalts also reflect variations in the mantle sources. Probably the only major element for which this is so is iron. If a basalt has only undergone fractional crystallization of olivine, then the abundance of FeO in the basalt reflects the FeO/MgO ratio of the mantle source, the degree of melting, and the pressure at which melting occurs. Relative pressures and degrees of melting can often be constrained, so that variations in the abundances of FeO can be used to obtain information about variations in the FeO/MgO ratio of the mantle sources of basalts.

Comparison of FeO contents with trace element and isotopic contents of basalts shows some striking correlations and leads to the following conclusions.

1. Parental magmas for Kilauean basalts from Hawaii may be related by different degrees of melting of a homogeneous, garnet-bearing source.

2. Mid-ocean ridge basalts from the North Atlantic show a negative correlation of La/Sm with FeO, suggesting that the sources that are most enriched in incompatible trace elements are most depleted in FeO relative to MgO, and are probably also depleted in the other components of basalt. This correlation does not apply to the entire suboceanic mantle.

3. A comparison of tholeiites from near the Azores and from Hawaii shows that sources with similar Nd and Sr isotope ratios may have undergone distinctly different histories in the development of their major and trace element abundances.

4. Ocean island tholeiites tend to be more enriched in FeO than ocean floor tholeiites. Either the ocean island sources have greater FeO/MgO ratios, or melting begins at significantly greater pressures beneath ocean islands than beneath ocean ridges.

5. Major element variations in the mantle are controlled mainly by tectonics and the addition or removal of silicate melts. Trace element variations, however, may be controlled by the addition or removal of fluids as well. Thus major elements, trace elements and isotopes may each give a different perspective important to the understanding of the evolution of the mantle.

Introduction

Trace element and isotopic studies of oceanic basalts suggest that the suboceanic mantle is heterogeneous with respect to certain trace element and radiogenic isotope ratios. Although the abundances of major elements in basalts have also been extensively studied, very little is known about mantle heterogeneity for the major elements, even though the major elements make up 99.5 % of the mantle sources of basalts. Major element heterogeneities do exist among ultramafic

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nodules. Ultramafic nodules, however, occur in relatively few rock types and may not be representative of the source regions of many basalts. Also, the mantle source of a basalt may include such a large volume that the heterogeneities documented by nodules might be averaged out. Since trace element and radiogenic isotope ratios in basalts do suggest large-scale heterogeneities in the mantle, it would be valuable to be able to determine the existence, magnitude and distribution of heterogeneities in the mantle by using major element abundances in basalts. It should then be possible to compare major element heterogeneities with trace element and isotopic heterogeneities.

TABLE 1. DEFINITION OF SYMBOLS USED

C_0^i	concentration of a given element *i* in the total system considered at the time that a given process begins
C_{L}^i	concentration of a given element *i* in the melt
C_{s}^i	concentration of a given element *i* in the total solid
C_{ol}^i	concentration of a given element *i* in olivine
C_{α}^i	concentration of a given element *i* in a mineral
F	the mole fraction of melt relative to the original or total system
$K_{\mathrm{d}_i}^{\alpha/\mathrm{L}}$	the mineral (α)-melt (L) distribution coefficient for a given element or component *i*, expressed in cation mole percentages; $K_{\mathrm{d}_i}^{\alpha/\mathrm{L}} = C_{\alpha}^i/C_{\alpha}^{\mathrm{L}}$
K_{D}	the exchange reaction distribution coefficient between olivine and liquid; it is the ratio of the K_{d}s for FeO and MgO (see text)

All concentrations are in cation mole percentages.
Primary magma: the composition of a liquid at the time that it is removed from the residue.
Parent composition: the composition of a system before melting.

This paper presents an evaluation of the effects of major element heterogeneity in the mantle upon the compositions of basalts. The evaluation demonstrates that the FeO contents of basalts can reflect variations in the FeO/MgO ratio in the mantle sources. Definitions of terms and symbols are given in table 1.

ELEMENTS IN BASALTS THAT REFLECT MANTLE HETEROGENEITY

The first problem is to determine which of the major elements in basalts could reflect mantle heterogeneity if it existed. Hanson & Langmuir (1978) defined three classes of elements with respect to modelling using single element distribution coefficients (K_{d}s): essential structural constituents, trace elements and intermediate elements. An essential structural constituent (e.s.c.) is an element that fully occupies one site in any mineral in the system considered. A mineral–melt K_{d} for this element specifies completely the abundance of the element in the melt, because the concentration of the element in the mineral is fixed. The abundance of the element in the melt varies only with K_{d}, so variations found in melts may reflect variations in K_{d} rather than variations in the parent composition. Thus, the distribution of e.s.cs between solid and melt is independent of both the abundance of the element in the system and the proportions of the phases present. Evaluating mantle heterogeneity for e.s.cs based on basaltic melt compositions is probably not possible, but e.s.cs can give valuable information on the minerals present and on the conditions of melting. Si, Ti, Al, Fe, Mg, Mn, Ca, Na, K and P are commonly included in major element analyses. Of these elements, Si, Ca, and Al are elements which are e.s.cs in most lherzolite–melt systems because they almost fully occupy sites in olivine, pyroxene, and garnet. Thus, they cannot be easily used for evaluating mantle heterogeneity.

A trace element follows Henry's Law in all phases, and is in such low abundance that it will not significantly affect the stability of the phases. Its abundance in a melt depends on the parent composition, the K_ds, the extent of melting and the phases present in the residue. Of the elements commonly included in a major element analysis, Ti, K, P and Mn may usually be treated as trace elements. For many trace elements, mantle heterogeneity is demonstrable (see, for example, Schilling 1973, 1975). Trace elements, however, may not be reliable indicators of major element heterogeneity in the mantle.

Na should behave as a trace element in mantle–melt systems and its abundance in primary magmas should reflect mantle heterogeneity because there is no known mineral in which it is an e.s.c.; its abundance in minerals is low; and the K_ds for Na based on experimental data (e.g. those of Bender *et al.* (1978) and Bultitude & Green (1971)) are quite low (no greater than 0.25), even for clinopyroxene at high pressures. Thus there should be significant variations in the abundances of Na in melts as a function of the extent of melting. This is generally not observed. For example, in basaltic glasses from the FAMOUS area, where trace elements with K_ds similar to Na (e.g. Ti, Sm) vary by a factor of 2, the abundance of Na varies by less than 10% (Langmuir *et al.* 1977). Two possible explanations for this perplexing problem would be (1) that Na has higher K_ds in mantle phases than has been demonstrated experimentally – e.g. a K_d for clinopyroxene–liquid of about 1.0 or greater would be necessary (the exact value depends on the melting process), or (2) that Na behaves as an e.s.c. in some mantle phase, e.g. jadeite. Na could be an e.s.c. if the jadeite component in pyroxene established its own equilibrium with the melt independent of the amount of the jadeite component in pyroxene. If this were so, then Al would also be an e.s.c. in a jadeite component. Owing to the problem of evaluating Na distribution during melting, it is difficult to evaluate Na heterogeneity in the mantle.

An intermediate element is an element that is in solid solution and does not completely occupy any one site in any mineral in the system but is abundant enough to be stoichiometrically important. The abundance of the element in a melt will be a function of the parent composition as well as the extent of melting and proportions of minerals present. The two remaining major elements, Mg and Fe, are intermediate elements in mantle–melt systems. Their abundances in basalts should reflect abundances in the sources, and thus the remainder of this paper concentrates on these two elements.

MgO–FeO DISTRIBUTION DURING MELTING AND CRYSTALLIZATION

Hanson & Langmuir (1978) showed how to model the distribution of FeO and MgO where olivine is present for melting and crystallization by using olivine–melt K_ds for FeO and MgO. FeO and MgO concentrations of melts and residues for melting of pyrolite (Ringwood 1975) are presented on an MgO–FeO diagram in figure 1. For a clear understanding of the utility and special features of Mg–FeO diagrams, the reader is referred to Roeder & Emslie (1970), O'Hara *et al.* (1975) and O'Hara (1976). Temperatures in figure 1 are based on olivine–melt K_ds for FeO and MgO in cation mole percentages at 1 atm† from Roeder & Emslie (1970). There are two fields, one for melts and the other for residues, and both fields are contoured with respect to the extent of melting and the temperature. Lines for fractional crystallization of olivine are superimposed on the melt field, with tick marks for each 5% crystallization of olivine.

The melt field in figure 1 is constructed for a single parent composition by using K_ds determined at one atmosphere on a restricted range of basaltic compositions. To establish mantle heterogeneity it must be demonstrated that a suite of basalts *cannot* be derived from a single

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† 1 atm ≈ 10^5 Pa.

parent composition, even if the K_ds vary widely as a function of pressure and melt composition, and even if the basalts have undergone differentiation. This requires a more detailed understanding of the dependence of FeO and MgO abundances in melts on K_ds and the exchange reaction distribution coefficient, K_D.

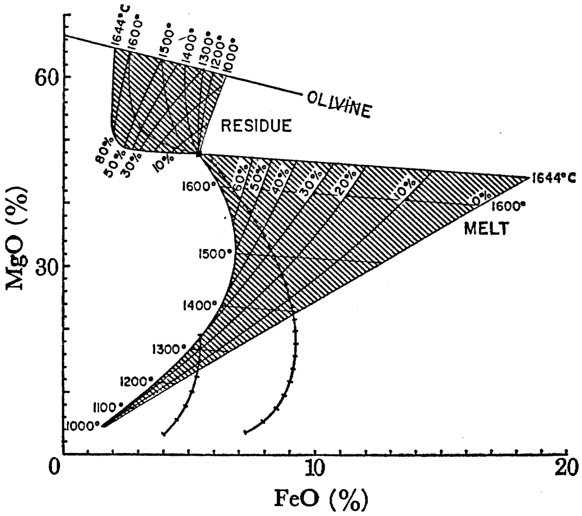

FIGURE 1. Plot of MgO against FeO in cation mole percentages with fields of melt and residue calculated by using the method of Hanson & Langmuir (1978). The parent composition is where the two fields meet.

Dependence of the melt field on K_D

K_ds for MgO and FeO vary widely as a function of melt composition and pressure, even at one temperature. For example, Roeder (1974) studied compositions where K_ds for MgO between olivine and melt vary by almost a factor of 2 at one temperature. Longhi *et al.* (1978), Leeman (1978) and Irvine & Kushiro (1976) also discuss compositional dependence. Hanson & Langmuir (1978), using data from the literature (Bickle *et al.* 1977; Longhi *et al.* 1978), showed a regular increase in K_ds for MgO and FeO with pressure. O'Hara (1976), Longhi *et al.* (1978) and Bender *et al.* (1978) also comment on a pressure effect.

In contrast to the K_ds, the exchange reaction distribution coefficient, K_D, shows little variation. For olivine–melt systems, K_D is defined as:

$$K_D = (C_{\text{ol}}^{\text{FeO}}\, C_{\text{L}}^{\text{MgO}})/(C_{\text{ol}}^{\text{MgO}}\, C_{\text{L}}^{\text{FeO}}). \tag{1}$$

K_D is simply related to K_ds as follows:

$$K_D = K_{\text{d, FeO}}^{\text{ol/L}}/K_{\text{d, MgO}}^{\text{ol/L}}. \tag{2}$$

Roeder (1974) and others have suggested the K_D stays relatively constant over wide ranges in composition because FeO and MgO are geochemically similar with respect to olivine–melt equilibria, and the compositional effects on the K_ds cancel out. K_D also seems to vary little with pressure. Bickle *et al.* (1977) found a K_D of 0.34–0.36 for olivine saturated melts (komatiites) at pressures from 30–40 kbar†. For terrestrial basalts, the maximum variation in K_D is probably 0.28–0.36. By using Roeder & Emslie's (1970) data at one atmosphere for tholeiites, K_D is nearly constant at values of 0.30 ± 0.01, which is in the middle of the expected range in K_D and is probably an appropriate value for most terrestrial basalts.

† 1 kbar = 10^8 Pa.

The relatively constant value of K_D is significant for evaluating mantle heterogeneity in FeO and MgO because the melt and residue fields on the MgO–FeO diagram are fixed by the value of K_D, as is shown by the following derivation. Given K_D and the abundances of MgO and FeO in the melt, the MgO and FeO abundances of the olivine in equilibrium with the melt can be determined from combining (1) with the stoichiometric equation for olivine,

$$C_{ol}^{MgO} + C_{ol}^{FeO} = 0.6667, \tag{3}$$

to yield

$$C_{ol}^{MgO} = 0.6667 C_L^{MgO} / (C_L^{FeO} K_D + C_L^{MgO}), \tag{4}$$

where 0.6667 is the mole fraction of octahedral cation sites in olivine since MgO and FeO abundances are then known in both melt and olivine, the K_ds for MgO and FeO are uniquely specified. As long as K_D is fixed, any given melt in equilibrium with olivine can thus have one and only one set of K_ds for MgO and FeO. These K_ds are independent of temperature, pressure, and the abundances of other components in the melt. They are determined only by K_D and the stoichiometry of olivine.

This concept can be extended from points to lines on the MgO–FeO diagram. Rearranging the definition of K_d from table 1,

$$C_{ol}^{MgO} = K_{d,\,MgO}^{ol/L}\, C_L^{MgO}, \tag{5}$$

and similarly for FeO. Substituting into (3) yields

$$K_{d,\,MgO}^{ol/L}\, C_L^{MgO} + K_{d,\,FeO}^{ol/L}\, C_L^{FeO} = 0.6667. \tag{6}$$

Rearranging and substituting into the definition of K_D leads to

$$C_L^{MgO} = -K_D\, C_L^{FeO} + 0.6667 / K_{d,\,MgO}^{ol/L}. \tag{7}$$

This is the equation for a line on an MgO–FeO plot with a slope of $-K_D$. For any line with a slope of $-K_D$, then from (7) and (2), $K_{d,\,MgO}^{ol/L}$ and $K_{d,\,FeO}^{ol/L}$ are constant at all points along the line. Along such a line the K_ds for FeO and MgO cannot vary even though temperature, pressure or the composition of the melts do vary. Lines with a slope of $-K_D$ may be called lines of constant K_ds. As changes in pressure and the abundances of components in the melt other than MgO and FeO affect the temperatures at which these K_ds occur, then points along a line of constant K_ds may represent different temperatures. The isothermal lines on Roeder & Emslie's (1970) olivine saturation surface and in figure 1 are lines of constant K_ds because pressure is fixed and it is assumed that there is no compositional dependence of the K_ds.

For a given parent composition, the positions of the contours for the extent of melting in the residue and melt fields on the MgO–FeO diagram (figure 1) are also dependent only on the value of K_D. For 0% melting, from the definition of K_D,

$$C_L^{MgO} = (C_{ol}^{MgO} / C_{ol}^{FeO})\, K_D\, C_L^{FeO}. \tag{8}$$

For a given parent composition, the composition of olivine is constant before melting, so if K_D is constant, (8) is an equation for one and only one straight line through the origin on a plot of MgO against FeO. The line is the 0% melting line.

The maximum extent of melting for any line of constant K_ds occurs when the composition of the residue reaches the line of pure olivine (figure 1). Mass balance then requires that for MgO,

$$C_L^{MgO}\, F + C_{ol}^{MgO}\, (1-F) = C_0^{MgO}, \tag{9}$$

and similarly for FeO. Solving the two mass balance equations for F, setting them equal and substituting from (1) yields:

$$C_{\mathrm{L}}^{\mathrm{FeO}} = \frac{(C_0^{\mathrm{MgO}} - C_{\mathrm{ol}}^{\mathrm{MgO}})\, C_{\mathrm{ol}}^{\mathrm{FeO}} - (C_0^{\mathrm{FeO}} - C_{\mathrm{ol}}^{\mathrm{FeO}})\, C_{\mathrm{ol}}^{\mathrm{MgO}}}{(C_0^{\mathrm{MgO}} - C_{\mathrm{ol}}^{\mathrm{MgO}}) - (C_0^{\mathrm{FeO}} - C_{\mathrm{ol}}^{\mathrm{FeO}})\, K_{\mathrm{D}}(C_{\mathrm{ol}}^{\mathrm{MgO}}/C_{\mathrm{ol}}^{\mathrm{FeO}})}, \tag{10}$$

and similarly for MgO. For each olivine composition, (10) specifies the melt composition. Equation (9) then gives F. The entire curve of maximum melting for any parent composition can thus be constructed based only on K_{D} and mass balance.

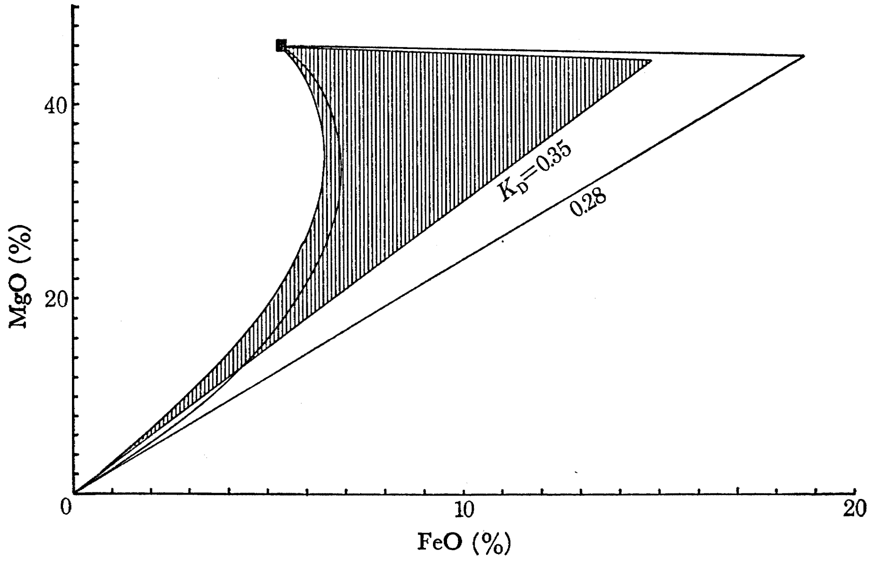

FIGURE 2. Effect of varying the exchange reaction distribution coefficient, K_{D}, on the melt field of the MgO–FeO plot in figure 1. The melt field in figure 1 is for $K_{\mathrm{D}} = 0.30$.

The fraction of melting contours for intermediate degrees of melting are also fixed by K_{D}. For any melt composition, the residue must plot on the extension of a line connecting the melt composition with the parent composition on the MgO–FeO diagram. The relation between residue composition and the composition of the olivine in the residue (Hanson & Langmuir 1978) fixes the point on the line, and mass balance then gives the degree of melting. Since this construction applies to any melt composition, the melting contours can be determined.

The curves of fractional crystallization of olivine alone can also be determined given only K_{D}. Olivine in equilibrium with a melt may be removed from the melt incrementally, with a new olivine composition calculated by using K_{D} at each increment (Roeder 1975).

By using K_{D} to construct the melt and residue fields without knowledge of K_{d}s, all information about temperature is lost. However, it does show that the contours of percentage melting for a given parent composition are valid over the pressure and compositional ranges of interest for terrestrial basalts, even though the temperature, pressure and compositional dependence of K_{d}s are not adequately understood. This is the key to evaluating mantle heterogeneity. The only ways to move the melt field significantly on the MgO–FeO diagram are to change K_{D} or to change the parent composition. Figure 2 shows the effects of varying K_{D} within the range of experimentally determined terrestrial compositions. In the cases that we consider, variations in K_{D} probably have no significant effect.

Effects of pressure on paths of melting

The position of the melt field on the MgO–FeO diagram is fixed independently of pressure for a single parent composition and a constant K_D. At a given pressure, however, the MgO and FeO contents of melts define a single curve across the melt field as the extent of melting increases. To evaluate how this path of melting varies with pressure, it is necessary to understand how K_ds vary with pressure. At any one temperature, K_ds for MgO and FeO increase with increasing pressure (Hanson & Langmuir 1978). This causes the temperature of a line of constant K_ds to increase by about 4–8 K/kbar. For example, data from Bickle *et al.* (1977) at pressures of 30 kbar suggest an increase of 6–7 K/kbar, and data of Bender *et al.* (1978) suggest a 4 K/kbar increase. We use a value of 6 K/kbar.

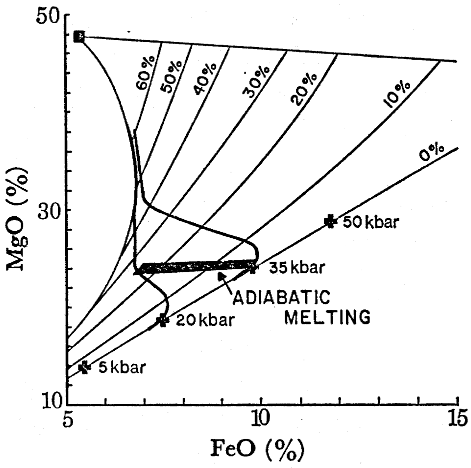

FIGURE 3. Estimated isobaric paths of melting across the melt field of the MgO–FeO diagram from figure 1 at 20 kbar and 35 kbar, based on data from Mysen & Kushiro (1977). The calculations of the paths are explained in the text. Also shown is an adiabatic path of melting where the solidus is first intersected at 35 kbar. The estimated positions of the solidi for dry melting are noted for 5, 20, 35 and 50 kbar.

According to Green (1976), the solidus temperature of a pyrolitic mantle increases by about 10–12 K/kbar. The increase is not linear over an extended pressure range, but 10–12 K/kbar may nevertheless be a good average value (Presnall *et al.* 1979).

The combination of the change in the temperature of the lines of constant K_ds with the change in temperature of the solidus results in increased MgO and FeO abundances for melts derived at higher pressures. For example, given a solidus temperature of 1200 °C at 1 atm, then from figure 1 the composition of the melt at the solidus (0% melting) is 4.5 mol % FeO and 11.4 mol % MgO. If the pressure is increased to 20 kbar, the solidus temperature is increased by 220 °C to 1420 °C, assuming an increase in the temperature of the solidus of 11 K/kbar. Since a line of constant K_ds increases by about 6 K/kbar, the 1420 °C isotherm for 20 kbar will have the same position as the 1300 °C isotherm for 1 atm. The solidus composition of the melt will then be about 6.6% FeO and 16.5% MgO. For a given extent of melting an increase in pressure causes MgO and FeO to increase in abundance in the melt by approximately 2% of the amount present for every kilobar and as is known this leads to melts that become more olivine normative with pressure. Relative to the isotherms at 1 atm, the position of the solidus increases by about 5 K/kbar. The relative positions of the solidus at 5, 20, 35 and 50 kbar are estimated in figure 3.

Isobaric v. *adiabatic melting*

For higher degrees of melting, the path of melting depends on how melting proceeds. The simplest melting is isobaric where heat is added to the system. This is the approach used in most experiments and might occur in the mantle if the heat for melting were supplied by radioactivity or by some external event such as magma intrusion. Estimated paths of isobaric melting shown in figure 3 are based on the experimental studies of Mysen & Kushiro (1977).

Another model for melting is in an adiabatically rising diapir, where the heat necessary for melting is internal to the system. Since the heat of fusion is supplied internally, temperature decreases as the extent of melting increases, which is the converse of the case for isobaric melting. To increase the extent of melting while decreasing the temperature requires a significant decrease in pressure. The extent of melting can be calculated as a function of the initial temperature and pressure, the latent heats of fusion, the relevant heat capacities, the change in the temperature of the solidus with pressure, and the extent of melting associated with an increase in temperature for a given pressure (see, for example, Cawthorn 1975). Turcotte & Ahren (1978) calculated that for an adiabatic mantle system, the heat of fusion requires a decrease in temperature of 100 K for 25% melting. Data of Mysen & Kushiro (1977) show that 25% melting occurs at a temperature about 40 K above the solidus. To melt a rising diapir by 25%, then, requires that the original temperature of the diapir at high pressure be 100 K + 40 K = 140 K above the lower pressure solidus where 25% melting eventually occurs. If the solidus temperature changes by 11 K/kbar and the adiabatic thermal gradient is 1 K/kbar, then 25% melting requires a pressure decrease of about 14 kbar.

As an example of a possible path of melting in an adiabatic diapir, consider that melting begins in a rising diapir at 1640 °C and 35 kbar. When the diapir has melted by 25%, the pressure must have decreased by 14–21 kbar, and the temperature must have decreased by 140 K to about 1500 °C. These extents of melting as a function of T and P are consistent with the data of Mysen & Kushiro (1977), who found 2% melting at 35 kbar and 1640 °C and 25% melting at 20 kbar and 1520 °C in two different sets of experiments on the same composition. The calculation of change in extent of melting with change in T and P can be combined with the melt-field of the MgO–FeO diagram to calculate a path of melting for a rising adiabatic diapir (figure 3). The temperatures for lines of constant K_ds decrease by about 6 K/kbar, so the 1640 °C line at 35 kbar is the 1550 °C line at 20 kbar. The temperature of the 25% melt at 20 kbar is 1500–1520 °C, *and lies approximately along the same line of constant* K_ds *as the* 2%, 35 kbar *melt*. These arguments suggest that at least for extents of melting up to 30–40%, the path of melting for an uprising diapir lies approximately along a line of constant K_ds. Diapirs intersecting the mantle solidus at higher pressures and temperatures have paths of melting lying along lines of constant K_ds at higher MgO contents than do diapirs intersecting the solidus at lower pressures and temperatures.

Melt compositions

Roeder (1974) and Leeman (1978) have noted that increased alkalis tend to increase the K_d for MgO (and probably FeO). Thus in a suite of melts representing different extents of melting from a common parent, e.g. from nephelinites to tholeiites, the higher alkalis in the melts derived by lower fractions of melting may reduce the differences in FeO among the melts and may lead to nephelinites with slightly lower MgO contents than would be expected for tholeiitic melts.

Water

In the calculation of the adiabatic path of melting on the MgO–FeO diagram, the temperature and pressure at which the adiabat intersects the solidus are crucial parameters. An increase in water content moves the solidus to lower temperatures for a given pressure, and a diapir with substantial water content would start melting at greater depth and would follow a higher pressure adiabatic path of melting on the MgO–FeO diagram than would a diapir with a lower water content. Mysen & Kushiro (1977), for example, show that addition of 1.99% H_2O to a mantle composition at 20 kbar decreases the solidus temperature by 25 K for a given fraction of melt in the range 5–40% melting. Owing to the relatively small effect of H_2O, however, the differences may not be noticeable.

Thermal heterogeneities

Thermal heterogeneities may also exist in the mantle because of the low thermal conductivity of lherzolite. On the basis of gravity anomalies, Cochran & Talwani (1978) suggest that there is a thermal anomaly of about +75 K beneath the North Atlantic. Thermal heterogeneities on smaller or larger scales may also exist and may be difficult to distinguish from chemical heterogeneities. A diapir with more heat, or possibly even a portion of a diapir with more heat, would intersect the solidus at higher pressure and temperature leading to melts with higher FeO contents for a given extent of melting than melts derived from a cooler diapir with the same chemical composition. A difference in temperature of 70 K will change the FeO abundance of a melt by 1% FeO.

Continuous melting

Continuous melting (Langmuir *et al.* 1977) may also be an important factor in the path of melting. It involves the continuous removal of melt as melting proceeds, with a portion of melt always remaining in the residue. The main effect is to change continuously the composition of the parent by removal of basaltic components, so the parent composition moves to lower abundances of FeO as melting proceeds (Hanson & Langmuir 1978). Continuous melting will thus cause a decrease in FeO abundances for a given extent of melting relative to batch melting and is a means of deriving melts with less FeO than the curve of maximum melting. Continuous melting may be tested by using rare earth elements (r.e.e.), which are more sensitive to this process.

Differentiation

Most basic or mafic melts which reach the Earth's surface have probably undergone some crystallization. Thus it is important to evaluate the extent of differentiation and the composition of the primary melts. This evaluation is straightforward on the MgO–FeO diagram for closed systems by using the melt field, the fractional crystallization lines for olivine, and subtraction lines for other phases.

Fractional crystallization of olivine can be evaluated by using the paths of crystallization on the MgO–FeO diagram (figure 1). They place limits on the composition of the melt from which the sample could have evolved through olivine crystallization. Crystallization of orthopyroxene, clinopyroxene and plagioclase all move melts to higher FeO contents than does crystallization of olivine. Fe–Ti oxide and garnet may deplete the melt in FeO, but for basic melts Fe–Ti oxide does not occur until late in the crystallization sequence, so unless garnet crystallizes alone over a considerable interval, the fractional crystallization line for olivine through a sample represents the maximum iron depletion possible through moderate amounts of fractional crystallization in a closed system.

O'Hara (1977) and others have suggested that fractional crystallization in a magma chamber periodically refilled with MgO rich melts may account for the chemical variations of oceanic basalts. These melts, however, would have olivine alone on the liquidus over a wide range in temperature, and olivine fractionation lines are almost vertical on the MgO–FeO diagram between 28 and 10 mol % MgO (20 and 7 % by mass). Thus the MgO contents of melts decrease rapidly with olivine fractionation, while the FeO contents do not vary. Even if they have undergone considerable fractional crystallization of olivine, the FeO contents of basalts that have olivine alone on the liquidus will still be representative of the primary magma, whether closed or open system fractional crystallization has taken place. A way to change significantly the FeO contents of basalts with olivine alone on the liquidus is to have them be mixtures of a very magnesian magma (28 mol % MgO) with a very evolved magma (4–6 mol % MgO). This extreme mixing process has not been shown to occur commonly. It is therefore possible that the FeO contents of many basalts with olivine alone on the liquidus may often be representative of the FeO contents of the more magnesian, parental magmas.

Changing parent composition

The discussion so far has been for a constant parent composition. To evaluate mantle heterogeneity it is necessary to understand the effects of changing the parent composition on the melt field and on the paths of melting on the MgO–FeO diagram.

For a constant K_D, the lines of constant K_ds are fixed regardless of the parent composition. The effect of a change in the parent composition is to move the melt field along the lines of constant K_ds. The changes in the melt field with changing parent composition may be summarized as follows (figure 4).

1. Decreasing the FeO/MgO ratio of the parent rotates the 0% melting line to a lower FeO/MgO ratio (see discussion of equation (8)).

2. Increasing the MgO content of the parent narrows the melt field. As the MgO content is increased, the parent composition approaches the line of olivine composition, reducing the maximum extent of melting possible along each line of constant K_ds.

3. Increasing the FeO content of the parent rotates the melt field about the origin to higher FeO/MgO ratios.

Clearly the position of the melt field reflects the FeO/MgO ratio of the parent composition. For evaluating mantle heterogeneity, the changes in the path of melting are as important as the changes in the melt field. For example, consider parent compositions A and B in figure 4, where the FeO/MgO ratio of A is less than that of B. We know that adiabatic paths of melting lie approximately parallel to the FeO axis. If the solidus temperature of A were not much higher than that of B, then points B1 and A2 would represent the solidi. For a given degree of melting, the FeO contents of melts would reflect the FeO/MgO of the parents. If, on the other hand, the solidus temperature of A were much higher than B, then points B1 and A1 would represent the solidi, and the FeO contents of melts would not vary with the FeO/MgO of the parents.

These two possibilities can be tested by using the data of Scarfe *et al.* (1979). They melted two lherzolites, with Mg/(Mg + Fe) of 0.89 and 0.93. The difference in temperature for a given degree of melting at 20 kbar was about 45 K, which would correspond approximately to a position of the solidus at point A3 in figure 4. Thus the FeO contents of melts decrease with decreasing FeO/MgO of the parent. This conclusion is supported by a comparison of Green's (1976) estimate of the solidus temperature of pyrolite compared with Mysen & Kushiro's (1977) determination of the solidus temperature of the ultramafic nodule PHN 1611.

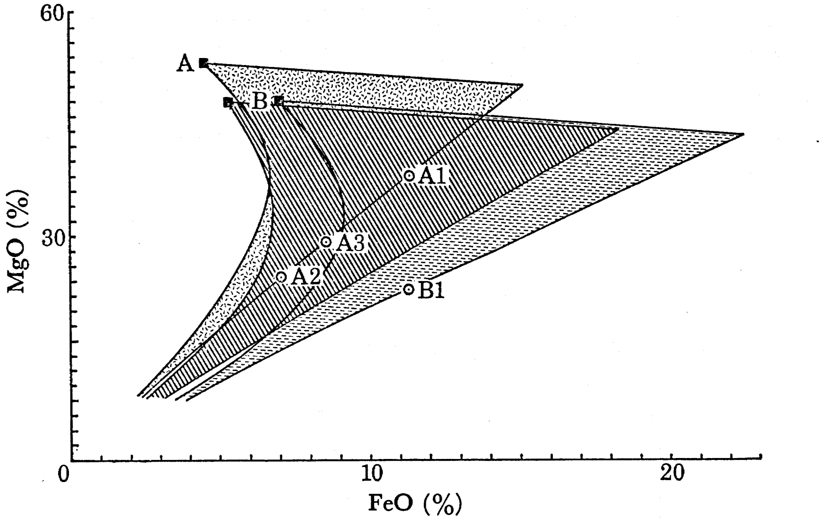

Figure 4. Effect of changing the parent compositions on the melt field. The field with slanted lines is the melt field from figure 1. The points marked A and B are discussed in the text.

Summary

The MgO and FeO contents of melts derived by batch melting of the mantle are affected by the pressure at which melting begins, the extent of melting, and the FeO/MgO ratios of the parent compositions. A variation of 1 mol% FeO may reflect: (1) a difference of 10% in the degree of melting (e.g. 5–15% or 10–20% melting); (2) a difference of about 7 kbar in the pressure (*ca.* 70 K in the temperature) at which melting begins; (3) a difference of about 1% in the forsterite content of the olivine in the peridotite parent (e.g. Fo$_{89}$ to Fo$_{90}$).

The abundance of MgO is so sensitive to olivine fractionation as to give little information about the MgO content of the primary magma. Since olivine fractionation lines are perpendicular to the FeO axis on the MgO–FeO diagram, the FeO contents of melts should reflect the FeO contents of the primary magmas, even if the melts have undergone considerable fractional crystallization of olivine. FeO contents of melts may thus be used as a petrogenetic indicator.

MgO–FeO HETEROGENEITY IN THE SUBOCEANIC MANTLE

In this section we shall consider the abundances of MgO and FeO for basalts from Hawaii (an intra-plate ocean island), the Azores (an ocean island near the Mid-Atlantic Ridge) and Iceland, and for ocean ridge tholeiites from the Mid-Atlantic Ridge. The purpose is to explore the possible uses of FeO as a petrogenetic indicator and to evaluate possible variations in the FeO/MgO ratio of the sources.

Because the Fe^{3+}/Fe^{2+} ratio in basalts is variable and it is uncertain whether the measured ratio reflects variations within the source or significant oxidation at higher levels, total Fe as FeO is used. Nonetheless, possible differences in the Fe^{3+}/Fe^{2+} ratio in the sources must be considered.

The Hawaiian and Azores Islands

The large, high quality data base for basalts from the Hawaiian Islands makes it possible to consider heterogeneities within the mantle sources for individual volcanoes as well as for the islands as a group. Wright and coworkers have studied extensively the tholeiites from Kilauea on Hawaii (Wright 1971; Wright & Fiske 1971; Wright *et al.* 1975) and they suggest that most of them can be related to several primary compositions. To compensate for the effects of differentiation, they normalize the compositions to constant MgO contents by addition or subtraction of olivine plus small amounts of chromian spinel (Wright 1971). After this normalization there is a total variation of about 1 mol % FeO among the samples. This variation would be equivalent to a minimum difference in extent of melting of about 10% if the lavas were derived by between 2 and 40 % melting from a homogeneous source (see figure 1). The difference in FeO is probably not a result of differentiation, because the pyroxene and olivine that could have affected the compositions of these rocks have FeO contents similar to the rocks themselves. The difference is probably not a result of plagioclase fractionation because plagioclase is not on the liquidus of the more magnesian rocks from Hawaii (Thompson & Tilley 1969; Wright & Fiske 1971). Variations in the Fe^{3+}/Fe^{2+} ratio might reduce the spread in FeO slightly.

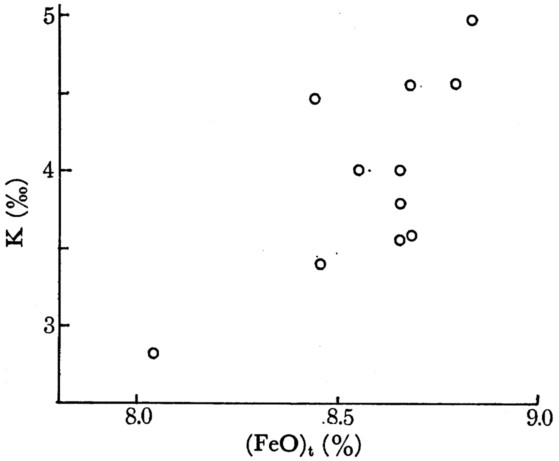

FIGURE 5. Plot of K against total iron as FeO in cation mole percentages for Kilauean summit lavas with MgO normalized to 7.0% by mass. Sources of data are Wright & Fiske's (1971) tables 6 and 9 and Wright's (1971) table 14.

A way of checking whether the range in FeO may be due to different extents of melting is to compare abundances of FeO with the abundances of a trace element such as K in least differentiated samples with constant MgO. Since K is most probably an incompatible element in tholeiitic melts, its abundance should be inversely proportional to the extent of melting. Figure 5 is a plot of K against FeO for the tholeiites from Kilauea. The observed positive correlation between K and FeO is what would be expected for a suite of basalts derived by different extents of melting. The total variation of K is 2800–4980 µg/g, or a factor of 1.76. If K is incompatible, this variation could be explained by a difference of a factor of 1.76 in the ratio of the extents of melting of the end members. We can calculate the range in extents of melting, because we have two unknowns (F_1 and F_2, the extents of melting for the end members) and two equations:

for FeO: $F_2 - F_1 = 10\%$;

for K: $F_2/F_1 = 1.76$.

The solution is $F_1 = 13\%$, $F_2 = 23\%$. These are minimum values of F. If the path of melting were not roughly parallel to the FeO axis, F_2–F_1 would be greater than 10%. The use of incompatible element and FeO variations together permits a rough estimation of the degrees of melting of a homogeneous source without assuming the abundances of either major or trace elements in the source. With the range in extent of melting known, the incompatible trace element content of the source could be determined for batch, continuous melting, or other models.

TABLE 2. TOTAL IRON AS FeO IN BASALTS FROM THE HAWAIIAN AND AZORES ISLANDS

	tholeiites	alkali basalts	basanitoids
Hawaiian			
Kaui	8.7	9.3	9.6
W. Maui	8.8	—	9.7
E. Maui	9.9	—	10.7
Oahu	8.4	—	9.9
Hawaii	9.9	—	—
Azores	6.6‡	7.4§	8.7§

† All data from MacDonald & Katsura (1964).
‡ Data from Schilling (1975).
§ Data from White (1977).

There is a consensus that the extent of melting increases in the sequence basanitoid to alkali basalt to tholeiite based on experimental studies (e.g. those of Green & Ringwood (1967) and Green (1970, 1973)) and trace element studies (e.g. those of Gast (1968), Kay & Gast (1973), Sun & Hanson (1975) and Frey *et al.* (1978)). If all of these rock types were derived from a parent composition with the same FeO/MgO ratio, the FeO contents of the rocks should decrease in the same order. Table 2 presents representative values of FeO for tholeiites and basanitoids from various volcanoes from the Hawaiian islands which have from 11–18 mol % (7–13 % by mass) MgO. Olivine or plagioclase fractionation or addition for these compositions probably has not affected the FeO content of the basalts because they have high Mg numbers (Mg/(Mg + Fe) on an atomic basis), plagioclase should not be on the liquidus, and the olivine fractionation lines for these compositions keep FeO essentially constant.

The basanitoids have a higher abundance of FeO than do the tholeiites and there is a difference of about 1% FeO between the two rock types (table 2). An undetermined amount of this difference may be due to increased ferric iron contents of the more alkalic rocks. Leeman (1978), however, has noted that increased alkalis tend to increase K_d for MgO (and probably FeO) at any one temperature. This would tend to minimize the difference in FeO between tholeiites and basanitoids and would make a small difference in FeO indicative of a larger difference in the extent of melting. Thus the effects of possible increased ferric iron content and increased K_ds for more alkalic melts work in opposite directions. If the 1% difference in FeO implies a minimum difference in extent of melting of 10%, and if the average degree of melting of the tholeiites is 17%, then the basanitoids are derived by less than 7% melting, which is consistent with Sun & Hanson's (1975) values of 5–10%. If melting were in an adiabatically rising diapir, the basanitoids would have separated from the source at a depth that is about 30 km deeper than the depth where the tholeiites separated. Within any one volcano, a source heterogeneous in MgO–FeO is not required, even though trace elements and isotopes may suggest heterogeneities (Tatsumoto 1978; Sun, this symposium).

When the tholeiites from Kilauea are compared with those from Mauna Loa, it is clear that more than different degrees of melting of a homogeneous source must be involved. Leeman *et al.* (1977) showed that the tholeiites from these two volcanoes have distinctive r.e.e. patterns which are not simply related to different degrees of melting of a common source. Tilley & Scoon (1961), Muir & Tilley (1963) and more recently Bence *et al.* (1979) have suggested that tholeiites from Kilauea and Mauna Loa follow two distinct liquid lines of descent. Of course, if the parent magmas for Kilauean tholeiites are derived by varying degrees of melting, then there are several liquid lines of descent just for the Kilauean tholeiites. In general, for the same MgO contents, the tholeiites from Mauna Loa are slightly lower in FeO and in incompatible trace elements than the lavas from Kilauea. Leeman *et al.* (1977) inferred a higher garnet/clinopyroxene ratio and greater depth of melting for the Mauna Loan sources relative to the Kilauean sources. If this were true, then Mauna Loan tholeiites should be relatively enriched in FeO rather than relatively depleted, if the degrees of melting were approximately the same. The lower FeO and incompatible trace elements may indicate a more depleted source for the Mauna Loan tholeiites relative to the source for the Kilauean tholeiites. If so, it would suggest that the tholeiites from two volcanos on the same island (Hawaii) may be derived from different sources.

The range of FeO contents among the Hawaiian Islands also could be interpreted as evidence for source heterogeneity. Tholeiites from some volcanoes are more FeO-rich than basanitoids from others. Within the basanitoids there is a range of FeO abundances of greater than 1%. If, as experimental and trace element evidence suggest, all the basanitoids are derived by less than 10% melting, then chemical heterogeneities or thermal differences are one possible explanation of the variation in FeO. A temperature difference of 100 K among adiabatic diapirs or significant differences in the FeO/MgO ratios of the sources would explain these data.

Figure 6 shows ultramafic nodules from Hawaii plotted on the MgO–FeO diagram where they can be compared with the field of residues for melting of pyrolite from figure 1. The nodules follow a trend from near olivine to a composition slightly richer in FeO than pyrolite. Assuming that the nodules are related to the basalts, the nodule data provide an important constraint on the sources of Hawaiian basalts. In general, Hawaiian basalts are enriched in FeO relative to ocean floor basalts for the same MgO content (figure 7). This enrichment could be due either to a greater depth of melting or to a source with a greater FeO/MgO ratio. If the FeO enrichment were exclusively a result of a greater depth of melting, the residues for Hawaiian basalts should be relatively depleted in FeO. If the nodules represent sources or residues for Hawaiian basalts, their high FeO contents suggest that the sources of Hawaiian basalts are enriched in FeO relative to sources of most ocean floor basalts. The ultramafic nodule PHN 1611 (Nixon & Boyd 1973) might have an appropriate major element composition for some of the Hawaiian sources, since it has about 1 mol % more FeO than pyrolite, but at the same MgO content.

The reasoning applied to the Hawaiian basalts may also be applied to FeO contents of basalts from the Azores Islands and the surrounding ocean floor (see table 2) (White 1977; Schilling 1975). The samples from the Azores Islands and surrounding ocean floor show a decrease in the total Fe in samples with high Mg/(Mg+Fe) from basanitoids (11–15% normative Ne) to alkali basalts (1–4% Ne) to m.o.r.b. from the Azores platform. The maximum difference in FeO for the Azores samples is 2.3 mol % (3% by mass), much greater than that observed for any single volcano from the Hawaiian Islands, but comparable to the entire range exhibited for the Hawaiian Islands (figure 7). For a given rock type, the basalts from the Azores have 2–3 mol % less FeO than do the Hawaiian basalts. This may be due to differences in temperature of up to 200 K or to differences in the FeO/MgO ratio of up to 50 % in the sources of Hawaiian and Azores basalts.

Alumina also is different in tholeiites from the two regions. Hawaiian tholeiites have about 12–14 % alumina by mass, while the tholeiites along the ocean ridge near the Azores tend to have about 16 % alumina. Experimental data on the partitioning of alumina between garnet and liquid suggest a K_d of about 2 (Bultitude & Green 1971). Since aluminium is an e.s.c. in garnet, and mantle garnets contain about 22 % alumina, a melt in equilibrium with garnet should contain about 11 % alumina, irrespective of the amount of garnet present. Thus the presence of garnet in the residue for Hawaiian tholeiites is a potential explanation of their low

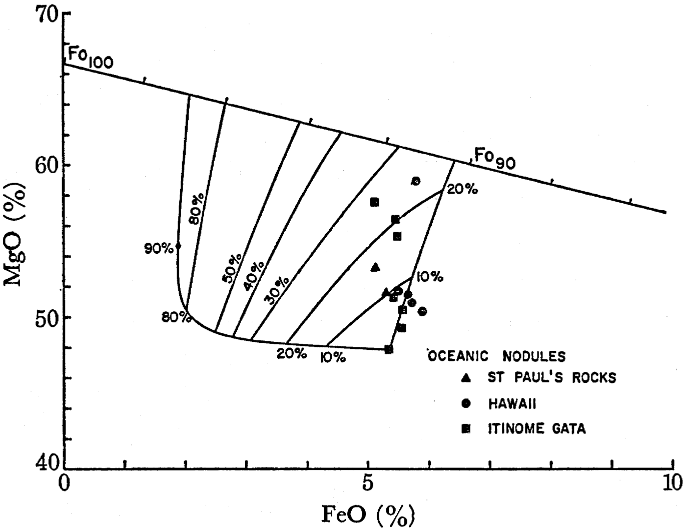

Figure 6. MgO and FeO abundances in cation mole percentages for ultramafic nodules from Hawaii. Allowance has been made for 5 % Fe_2O_3. Data are from Kuno (1969), Kuno & Aoki (1970) and Melson *et al.* (1967).

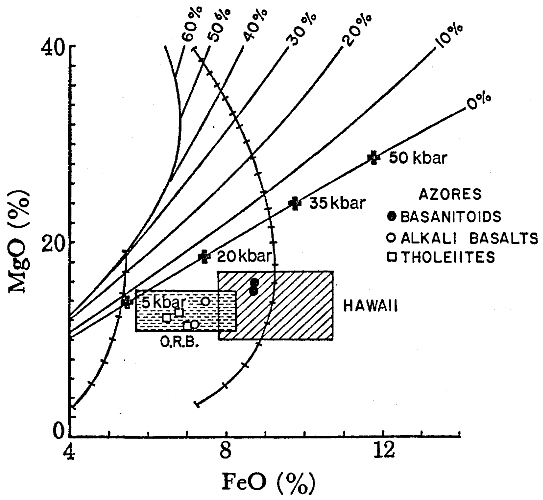

Figure 7. Plot of MgO against total iron as FeO in cation mole percentages for basalts from the Azores Islands and neighbouring ocean floor (Schilling 1975; White 1977), from the Hawaiian Islands (MacDonald & Katsura 1964) and from the Atlantic Ocean floor (Bryan & Moore 1977; Frey *et al.* 1974; Schilling 1975; Wood *et al.* 1979). The Hawaiian and Atlantic data were selected to exclude potential cumulates and more differentiated samples. Also shown is the melt field from figure 1.

alumina contents. If the tholeiites from near the Azores have not undergone large extents of fractional crystallization, the high alumina contents of the tholeiites from near the Azores suggest that garnet may not have been a residual mineral. Since garnet is a relatively high pressure mantle phase, this suggests that the Hawaiian tholeiites may have separated from the mantle at higher pressures than the tholeiites near the Azores. Alternatively, the mantle source for the Azores tholeiites may have been sufficiently depleted in basaltic components that all the garnet was melted out of the source. In any case, owing to the very large differences in FeO, the source for the Hawaiian basalts is probably more enriched in iron than that for the Azores basalts.

A comparison of the data from Hawaiian tholeiites and tholeiites near the Azores is instructive because it shows some of the complexities involved in evaluating mantle heterogeneity. Tholeiites from both areas are above proposed mantle plumes and have similar $^{87}Sr/^{86}Sr$ isotope ratios (White & Schilling 1978; O'Nions *et al.* 1977). The tholeiites from near the Azores appear to come from a source that is currently light-r.e.e. enriched (White & Schilling 1978), has a time-averaged history of light-r.e.e. depletion, and is relatively depleted in FeO. In contrast, the Hawaiian tholeiites appear to come from a source that is *not* enriched in the light r.e.e., has a time-averaged history of light-r.e.e. depletion, yet is relatively enriched in FeO. Clearly, very different processes, or sequences of processes, have been involved in the petrogenesis of these rocks. Assuming that the mantle was initially homogeneous, one possibility would be that the Hawaiian tholeiites lost a portion of their light r.e.e. at some time in the past, but did not lose a significant major element component. Melting of the source leaving garnet as a residual phase might lead to the major and trace element and isotopic characteristics of the tholeiites. In contrast, the sources of the tholeiites from near the Azores have lost a significant major element component leading to depletion in FeO, and have undergone relatively recent enrichment in the light r.e.e. This source was then melted without leaving garnet as a residual phase. These two scenarios would lead to the differences in FeO, Al_2O_3, r.e.e. and isotopic contents of the tholeiites from Hawaii and from near the Azores. The crucial point, however, is that sources with similar radiogenic isotope ratios appear to have undergone quite different histories.

The Reykjanes Peninsula

Jakobsson *et al.* (1978) have shown that basalts from the Reykjanes Peninsula have large variations in major and minor element chemistry which correlate with age. Zindler *et al.* (1979) have studied the Nd and Sr isotopes and the r.e.e. in these samples. They show that the basalts come from heterogeneous sources and suggest that the suite of samples results from mixing of two isotopically and chemically distinct magmas. Figure 8 is a plot of $(La/Sm)_N$ against FeO for these samples. There is a positive correlation between La/Sm and FeO from 8.5 to 11% FeO, which may be a result of mantle heterogeneity or the conditions of melting. $(La/Sm)_N$ remains approximately constant for samples with greater than 10% FeO, which would be consistent with an origin through low pressure fractional crystallization involving plagioclase for the higher FeO samples. Zindler *et al.* (1979) suggest from the r.e.e. and isotopic evidence that the high FeO, high La/Sm melts are derived from lower degrees of melting at higher pressures than are the melts with low FeO and low La/Sm ratios. The FeO abundances would be consistent with this model, since higher pressure and lower degrees of melting would both tend to increase the FeO contents of melts. Previous depletion of the source leading to lower FeO abundances and lower La/Sm ratios would also contribute to the positive correlation between La/Sm and FeO.

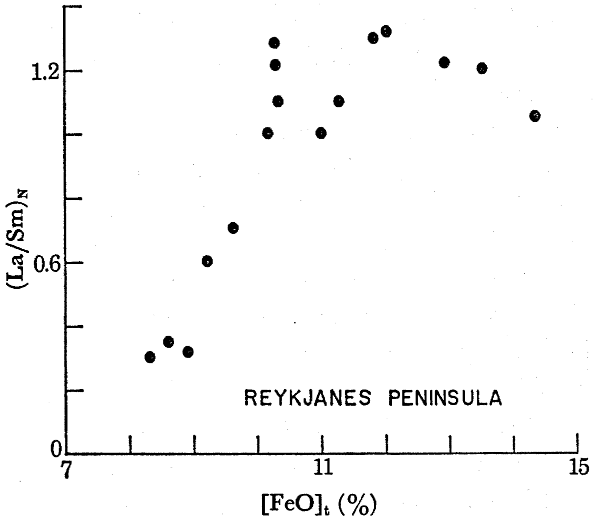

FIGURE 8

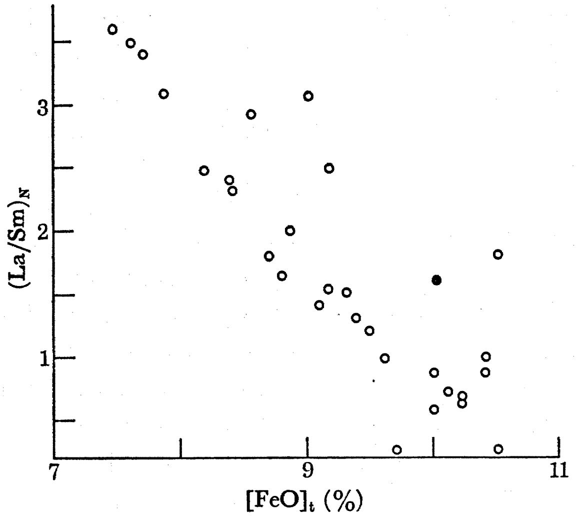

FIGURE 9

FIGURE 8. Total iron as FeO in percentages by mass against chondrite-normalized La/Sm ratio $(La/Sm)_N$ = $(0.61 \times La/Sm)$. Data are from Jakobsson *et al.* (1978) and Zindler *et al.* (1979).

FIGURE 9. Total iron as FeO in percentages by mass against the chondrite normalized La/Sm ratio for basalts with greater than 8 % MgO from the Mid-Atlantic Ridge in the North Atlantic. Data are from Schilling (1975), Wood *et al.* (1979) and Langmuir *et al.* (1977). The filled circle has undergone minor plagioclase fractionation, which would result in enrichment in FeO, yet has more than 8 % MgO (sample 526–5 from Langmuir *et al.*).

Mid-Atlantic Ridge tholeiites

The tholeiites from the Mid-Atlantic Ridge near the Azores are as a group distinct from the alkali basalts and basanitoids on the Azores. However, these tholeiites show variations in isotope and trace element ratios among themselves (Schilling 1975), and there are even larger variations between the tholeiites near the Azores and those from further south along the ridge. Schilling (1975) analysed basalts dredged at intervals along the Mid-Atlantic ridge between 30° N and 45° N. In these samples there is a positive correlation between $(La/Sm)_N$ and $^{87}Sr/^{86}Sr$ and a rough correlation between either of these ratios and distance from the Azores platform (White & Schilling 1978). The question arises whether the variations in these trace element and isotope ratios are reflected in the major elements compositions of the basalt sources.

Total Fe as FeO is plotted against $(La/Sm)_N$ in figure 9 for all tholeiites with greater than 8 % MgO by mass analysed by Schilling (1975) from the ridge south of the Azores and by Wood *et al.* (1979) and Langmuir *et al.* (1977) between 30° N and 45° N. The negative correlation between total FeO and the $(La/Sm)_N$ ratio suggests that the sources most depleted in incompatible trace elements may be most enriched in FeO and presumably enriched in basaltic components.

Some samples with greater than 8 % MgO by mass have not been plotted in figure 9. Those samples that Schilling reports to be extensively altered and contaminated with sediment are excluded. Wood *et al.* (1979) report that one of their samples contains 20 % plagioclase megacrysts. The presence of megacrysts would cause the abundance of FeO in the rock to be lower than that of the melt. When the FeO abundance is corrected for the amount of megacrysts, the sample lies in the field of the correlation. Langmuir *et al.* (1977) suggested that light r.e.e. in some samples from the FAMOUS area at 36° N along the Mid-Atlantic Ridge had been depleted by a continuous melting process in the mantle which could also deplete the FeO abundances.

Those samples from the 36° N area with light-r.e.e. depleted patterns (Langmuir *et al.* 1977; Wood *et al.* 1979) do not fall in the field of the La/Sm–FeO correlation, while those that are light-r.e.e. enriched do lie in the field of the correlation.

The negative correlation on the La/Sm–FeO diagram occurs despite effects that work against it. The first is ferric iron. Basalts with high La/Sm ratios usually have more Fe_2O_3 than those with lower ratios, which would relatively inflate their total Fe contents since all Fe is considered as FeO. Secondly, trace-element enriched basalts that have high La/Sm ratios are generally believed to be derived by lower degrees of melting, which should lead to higher FeO contents. Thirdly, plagioclase fractionation would lead to increased FeO contents of melts while having little effect on the La/Sm ratios. In spite of these factors, which would tend to obscure or destroy a negative correlation between La/Sm and FeO, a negative correlation is observed.

O'Hara (1977) has suggested that variations in oceanic basalts might be accounted for by processes acting in a periodically refilled magma chamber. The La/Sm–FeO correlation is one of the features of m.o.r.b. chemistry that cannot be easily accounted for by such processes. Fractional crystallization of m.o.r.b. leads to iron enrichment. If O'Hara is correct in stating that a periodically refilled magma chamber can lead to large increases in La/Sm, then magmas coming from such a magma chamber should show a positive, rather than a negative, correlation between La/Sm and FeO.

If the FeO variations reflect differences in the parental magmas, then these differences may result from differences in the pressure of melting or mantle heterogeneity. If the negative correlation results from pressure differences, and the mantle sources have similar FeO/MgO ratios, then differences in FeO content require a difference in pressure of 20 kbar, which would suggest large temperature differences among the sources. If the FeO differences are a result of different depths of melting, then the sources melting at the greatest depth would have the lowest La/Sm ratio. The overall similarity of most major elements in m.o.r.b. leads us to believe that different depths of melting are not the primary cause of the variations in FeO.

Instead, the La/Sm–FeO correlation most probably represents variations in both the FeO/MgO and La/Sm ratios in the mantle sources. If so, there are significant implications for the development of heterogeneities in the mantle sources of North Atlantic basalts. Those parts of the mantle beneath the North Atlantic that have lower FeO/MgO ratios have higher La/Sm ratios, while those parts with the highest FeO/MgO ratios have the lowest La/Sm.

Assuming that the mantle was originally homogeneous, the main process that could cause a change in the major element composition of a mantle source would be melt removal or melt addition before the melting that produced the tholeiites found at the ridge. Addition or removal of melt would lead, respectively, to increased or lowered FeO/MgO ratios of the source. The addition or removal of melt would also lead, respectively, to increased or lowered La/Sm ratios of the source, resulting in a positive correlation between FeO/MgO (or FeO) and the La/Sm ratio. The observed negative correlation suggests that another process, or a combination of processes, may be involved. One possible process would be a non-silicate fluid phase. Lloyd & Bailey (1975) found evidence for metasomatism in the subcontinental mantle and they and others have suggested that a fluid phase may transfer elements within the mantle, changing trace element abundances and ratios, without significantly affecting major element abundances. This might be expected to lead to a random relation between major and trace element heterogeneities rather than the observed negative correlation.

Any model for the origin of the heterogeneous sources of m.o.r.b. in the North Atlantic must be compatible with both the major and trace element evidence. Normal ocean ridge basalts from the northern Mid-Atlantic Ridge are depleted in incompatible elements, but seem to come from the source with the highest FeO/MgO ratio. The sources of these basalts may have lost a fluid phase or small degree of melt, but probably not a significant amount of silicate melt. If so, this might explain why the sources that seem most depleted on the basis of trace element ratios are such voluminous producers of tholeiitic basalts. Ocean ridge tholeiites from near the Azores, which are generally more enriched in incompatible trace elements and radiogenic isotopes, are apparently derived from sources that may have lost a significant melt fraction, resulting in a lower FeO/MgO ratio. They may have undergone a later enrichment event which added incompatible trace elements but did not add a significant amount of basaltic components. The enrichment event may be consistent with an incompatible-element enriched silicate liquid, or fluid phase.

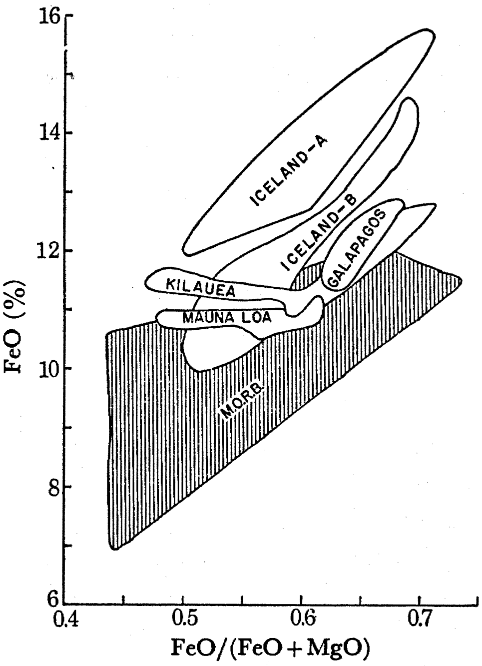

Figure 10. Total iron as FeO in percentages by mass against FeO/(FeO+MgO) in percentages by mass for ocean floor basalts from the Mid-Atlantic Ridge and the Nazca Plate and for selected ocean island basalts. Sources of data are: McBirney & Williams (1969), Sigurdsson & Schilling (1978), MacDonald & Katsura (1964), Muir & Tilley (1963) and Tilley & Scoon (1961). Iceland-A is for basalts from Skagi. Iceland-B is for basalts from Langjökull.

A general comparison can be made between ocean island tholeiites and ocean floor tholeiites. Figure 10 is a plot of FeO/(FeO+MgO) against FeO comparing fields for tholeiites from various ocean islands and m.o.r.b. There are clearly some variations. More importantly, ocean floor basalts generally plot below the ocean island fields, although there is some overlap. This would suggest that either the ocean island tholeiites melt at greater depths, and thus are derived from regions of the mantle with positive thermal anomalies, or that the FeO/MgO ratios are generally higher for the mantle sources for ocean island tholeiites than for sources of ocean floor tholeiites.

The correlation that we have observed for the tholeiites from the North Atlantic cannot be extended indiscriminately to the suboceanic mantle as a whole. The data from the Reykjanes

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Peninsula show a positive correlation between La/Sm and FeO; ocean island tholeiites seem to be generally enriched in FeO; and there is some indication that m.o.r.b. from other areas of the ocean floor do not fall in the field of the correlation. The data from regions of the ocean floor other than the Mid-Atlantic Ridge near the Azores will probably need to be unravelled by detailed work on well characterized, carefully selected samples. We emphasize, however, that the data from the Azores region appear to document mantle heterogeneity in as well as an inverse correlation between, the FeO/MgO and La/Sm ratios on a scale of thousands of kilometres Although this correlation may not apply to the entire suboceanic mantle, it is not unique to the northern Mid-Atlantic Ridge. Frey & Green (1975) and Frey & Prinz (1978) have shown that ultramafic nodules from the subcontinental mantle also have a negative correlation between enrichment in basaltic components and enrichment in La/Sm.

CONCLUSIONS

The following generalizations can be made about MgO–FeO heterogeneity in the suboceanic mantle.

1. The FeO contents of basaltic liquids that have undergone crystallization only of olivine are dependent on the pressure at which melting occurs, the extent of melting and the FeO/MgO ratio of the mantle source.
2. There are variations in the FeO/MgO ratio of the mantle sources of oceanic basalts. Since FeO/MgO varies, variations in other major elements may also be expected.
3. Major and trace element heterogeneities may be either positively or negatively correlated, suggesting variable and complex histories for the mantle sources of oceanic basalts.
4. Although the Hawaiian Islands and the Azores Islands have similar Nd and Sr isotopic ratios, their respective sources appear to have undergone distinctly different histories.
5. Tholeiites from ocean islands have higher FeO contents than tholeiites from the ocean floor for similar FeO/MgO ratios. These differences reflect either thermal anomalies beneath ocean islands, causing a much greater depth of melting, or higher FeO/MgO ratios in the sources of ocean island tholeiites. The ocean islands appear to have sources which have variable FeO/MgO ratios or conditions of melting within a given island as well as from island to island.
6. When variations in the FeO/MgO ratio of the mantle sources are compared with variations in trace element ratios, the conclusion is reached that trace elements may move independently of major elements in the mantle. Trace element and radiogenic isotope ratios may be reflecting a history of migration of both fluid phases and silicate melts through the mantle. Major element heterogeneities, on the other hand, may be reflecting primarily a history of silicate melt migration. Thus major elements, trace elements and isotopes give different perspectives and can be used together to give a more comprehensive view of the evolution of the mantle.

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Discussion

M. J. O'Hara (*Department of Geology, Llandinam Building, University College of Wales, Aberystwyth, Dyfed. U.K.*). I wish to draw the authors' attention to some earlier attempts to treat the MgO–FeO balance during partial melting and subsequent fractionation (O'Hara *et al.* 1975; O'Hara 1976, pp. 106–107) which support the view that komatiite has been extracted from an orthopyroxene-bearing residuum. Similar conclusions concerning the changing nature of the residuum with the pressure of the partial melting events which are developed graphically in the second of these publications are similar to those which can be derived from the authors' figures.

I should like to investigate further the proposition that m.o.r.b. cannot be derived by olivine fractionation from komatiite or the Baffin Bay picrites. In closed system fractionation, and accepting all assumptions and calculations to be correct, the authors' figures indicate that this will be true.

It is qualitatively obvious that fractionation of olivine in a magma chamber in which new batches of primary komatiite or picrite magma were being regularly added will produce fractionation trends that evolve to lower FeO values with reducing MgO than the closed system paths which you show. The final constraints are that in the steady state, with small values of X and Y (see O'Hara 1977), the composition of m.o.r.b. must be approached along the tangent to the closed system fractionation curve passing through m.o.r.b.

Provided the komatiite and picrite parent magmas fall to the FeO-poor side of that tangent extended, then there will exist some combination of the parameters X, Y, Z which will permit m.o.r.b. to be the derivative of komatiite or picrite by olivine fractionation alone.

The questions then are: (*a*) whether or not the required parameters X, Y, Z are acceptable on geological grounds (a highly subjective judgement), and (*b*) what constraints are imposed on the source composition by the requirement that the primary magma lie on or to the FeO-poor side of the tangent to the closed system fractionation line passing through m.o.r.b.?

C. H. Langmuir and G. N. Hanson. We are grateful to Professor O'Hara for pointing out his 1976 publication, of which we had not been aware. Both O'Hara *et al.* (1975) and O'Hara (1976) use mass balance and the MgO–FeO diagram to relate primary melts to residual compositions and mineral assemblages. Our papers on the subject build upon the excellent base established for the MgO–FeO diagram by O'Hara *et al.* (1975) and Roeder & Emslie (1970).

An important problem is the origin of the MgO and FeO contents of ocean ridge basalts (m.o.r.b.). O'Hara *et al.* (1975) suggested on the basis of mass balance calculations that m.o.r.b. could not be close to primary magmas and must be derived from significantly more FeO-rich and MgO-rich liquids. Hanson & Langmuir (1978) showed that these conclusions resulted from the use of FeO-poor harzburgites from the subcontinental mantle as residual compositions;

that partial melting calculations show some m.o.r.b. may be close to primary, having undergone only moderate amounts of olivine fractionation; and that the compositions of ultramafic nodules from the suboceanic mantle are suitable residua for primary m.o.r.b. with about 15–16% MgO.

These discussions applied to closed system fractionation. To respond to Professor O'Hara's suggestion that open system fractionation may relate Baffin Bay compositions to m.o.r.b. compositions requires some calculations. Crystallization of olivine and plagioclase have been calculated by using a method for modelling major elements that permits modelling of plagioclase–olivine–melt equilibria for m.o.r.b. compositions in close agreement with experimental data on dry systems at one atmosphere (Langmuir & Hanson, in preparation).

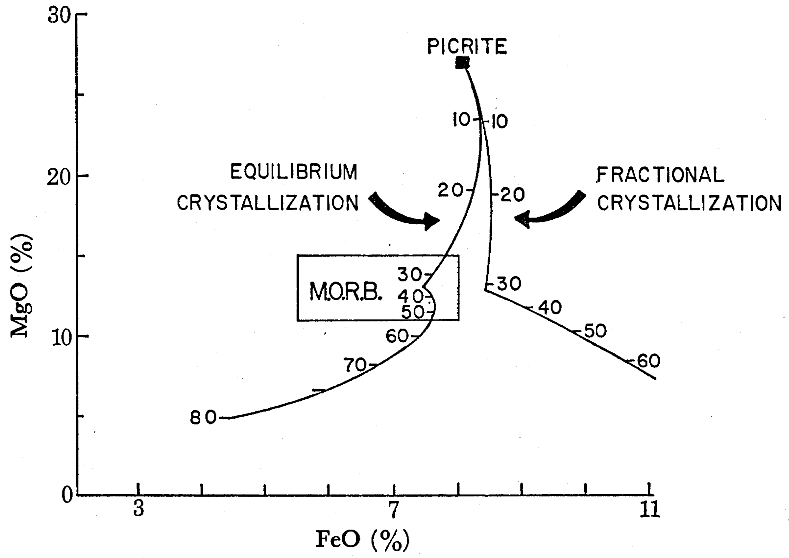

FIGURE 11

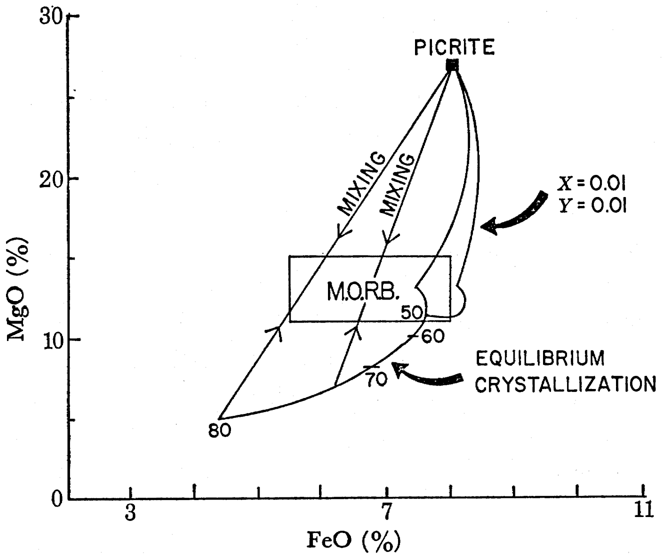

FIGURE 12

The Baffin Bay picrite composition given in O'Hara *et al.* (1975) was selected as the starting composition, and the open-system process suggested by Professor O'Hara was modelled for various values of the fraction crystallized (X) and the fraction erupted (Y), with a sufficient number of cycles for the liquid in the magma chamber to reach a steady state. In the steady-state condition the composition of the magma is not constant, but varies between its composition 'after crystallization' and its composition 'after mixing'. For very small values of X and Y these compositions converge. Equilibrium crystallization was used in the calculations because it leads to more FeO-poor compositions than does fractional crystallization, and is more effective in relating the Baffin Bay picrite to m.o.r.b. (figure 11).

The principal result of the calculations is that, regardless of the values of X and Y, the steady-state composition 'after crystallization' lies along the equilibrium line of descent of the initial, parent liquid. This is true for *all* elements. If X and Y are small, then even 'after mixing' the liquid deviates very little from the equilibrium line of descent once a steady state is reached. The position of the steady state along the equilibrium line of descent is fixed by the proportion $X/(X+Y)$. The proportion $X/(X+Y)$ is equal to the amount of crystallization that would lead to the same liquid composition in the closed system. The number of cycles necessary and the path of the liquid taken to reach a steady state are determined by the magnitude of X and Y.

These statements may be illustrated as follows. Figure 11 shows the liquid lines of descent for equilibrium and fractional crystallization of olivine and plagioclase from the Baffin Bay picrite in a closed system. Figure 12 shows the path that the liquid takes to reach a steady state when $X = Y = 0.01$ for equilibrium crystallization in an open system process. Since $X/(X+Y) = 0.5$, the steady-state composition is the same as 50% crystallization in a closed system, and the same steady-state composition would be reached for any magnitude of X and Y, as long as $X = Y$. The open system path barely intersects the most FeO-rich end of the m.o.r.b. field.

From these calculations, the Baffin Bay picrite could be parental to the most FeO rich m.o.r.b. It could give rise to the MgO and FeO contents of all m.o.r.b. only if the following conditions were met (figure 12). (1) Equilibrium rather than fractional crystallization occurs. (2) X/Y varies systematically between 1 and 4. (3) $X+Y$ must be less than 0.25 when $X/(X+Y) = 0.5$, or else mixed magmas would be too MgO-rich at 7.5% FeO. $X+Y$ must be between 0.28 and 0.50 when $(X/(X+Y) = 0.8$, or else mixed magmas would not have the correct MgO abundances at 6 mol % FeO. (4) FeO-poor m.o.r.b. magmas must be erupted only 'after mixing' with incoming magmas, and not 'after crystallization'.

It should also be noted that if X and Y are small, and if equilibrium crystallization occurs, there will be no excess enrichment of trace elements in the steady state relative to the equilibrium line of descent in the closed system.

Consideration of three additional factors argues against such a scenario. First, in all probability crystallization is somewhere between the equilibrium and fractional end members. O'Hara (1977) used fractional crystallization as the basis of his arguments. As is evident from figure 11, this would lead to FeO enrichment, away from the m.o.r.b. field. Another factor leading to FeO enrichment would be inclusion of pyroxene in the calculations. Finally, comparisons of the normative albite and anorthite contents of Baffin Bay picrite and m.o.r.b. show that the conditions that account for MgO and FeO cannot account for normative albite and anorthite.

Even if these additional considerations are ignored, it would require a bizarre coincidence of conditions for m.o.r.b. magmas to be derived from a single composition similar to Baffin Bay picrite. The Earth's mantle must have undergone a complex history, caused by accretion, core and continent formation, and gigayears of convection and mafic rock generation. Could such a history lead to anything other than a heterogeneous mantle? Melts derived from a heterogeneous mantle, under a range of melting conditions, will themselves be heterogeneous. The MgO and FeO contents of the Baffin Bay picrite suggest that it may have been derived at greater pressures, or from a source richer in FeO than the sources of most m.o.r.b.