

## High pressure phase equilibrium constraints on the origin of mid-ocean ridge basalts\*

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**Abstract**—A search of about 1700 analyses of abyssal basalt glasses has produced a set of 40 very primitive compositions with *mg* numbers greater than 70. None are picritic. On an olivine-plagioclase-quartz normative triangle, the primitive compositions form an array elongated toward the quartz apex that mimics the array of abyssal basalt glasses in general. Fractional crystallization with or without magma mixing would produce residual liquids with lower *mg* numbers and higher concentrations of K<sub>2</sub>O, TiO<sub>2</sub>, and Na<sub>2</sub>O than the parental magma. When these changes are used to test the suitability of various experimentally produced basaltic liquids as parental magmas to the primitive glasses, we find 9 suitable analyses synthesized at 10 kbar and one at 5 kbar. The compositions of these parental basalts are either close to those of the primitive glasses or fall within the field of the primitive MORB glass array. Picritic liquids produced to date at pressures above 15 kbar do not have sufficiently high *mg* numbers and sufficiently low TiO<sub>2</sub>, Na<sub>2</sub>O, and K<sub>2</sub>O contents to be parental, but this may indicate only that the appropriate experimental conditions have not yet been found.

Melting relationships from 1 bar to 20 kbar for simplified lherzolite in the system CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-Na<sub>2</sub>O indicate that at pressures below 9.6 kbar where plagioclase lherzolite is stable, the composition of the liquid changes little with degree of melting up to 19 (at 0 kbar) to 32 (at 9.6 kbar) percent liquid. Above a transition interval from 9.6 to 10.8 kbar, spinel lherzolite is stable, and the liquid composition changes more rapidly with percent melting from an alkalic composition below about 10 to 25% melting (depending on pressures) to a tholeiitic composition at higher melting percentages. For amounts of melting of simplified lherzolite less than about 5 to 15%, picritic primary magmas cannot be parental to any of the primitive mid-ocean ridge basalt glasses, and only if the maximum amount of melting is greatly in excess of 20 to 30% could picritic magmas be parental to the entire array of primitive MORB glasses. However, these very large amounts of melting exceed estimates based on trace element considerations. The phase relationships support a model involving generation of primary non-picritic magmas throughout the pressure interval 5–11 kbar coupled with polybaric fractional crystallization as the magmas ascend to the earth's surface. The majority of primary magmas appear to be generated at about 9 to 10 kbar where a low-temperature region occurs on the simplified lherzolite solidus.

### INTRODUCTION

THE COMPOSITION and depth of origin of primary mid-ocean ridge basalts has been a matter of continuing debate. Some have advocated picritic primary magmas generated at pressures of about 15–30 kbar (O'HARA, 1968; GREEN *et al.*, 1979; STOLPER, 1980; JAUQUES and GREEN, 1980; ELTHON and SCARFE, 1984; ELTHON, 1986), whereas others have advocated primary magmas generated at pressures of about 7–11 kbar that have non-picritic compositions similar or identical to the most primitive lavas observed at mid-ocean spreading centers (GREEN and RINGWOOD, 1967; KUSHIRO, 1973; PRESNALL *et al.*, 1979; FUJII and BOUGAULT, 1983; TAKAHASHI and KUSHIRO, 1983; FUJII and SCARFE, 1985; PRESNALL and HOOVER, 1984, 1986).

In this paper, we focus on the generation and crystallization of the most primitive mid-ocean ridge basalt (MORB) glasses because they represent the best candidates for primary magmas that have reached the earth's surface. The paper is divided into two main parts. We first compare the compositions of primitive MORB glasses to liquid compositions produced from existing melting experiments on natural starting materials in order to determine which of these experimentally produced liquids could represent magmas parental to the primitive glasses. Then we present new experimental data on melting relationships of simplified lherzolite in the system CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-Na<sub>2</sub>O (CMASN) from 1 bar to 20 kbar and discuss the bearing of these data on the generation and crystallization of primitive MORB glasses.

### PRIMITIVE MORB COMPOSITIONS

As a criterion for a primitive MORB glass, we require that the *mg* number [ $mg = 100 \text{ Mg}/(\text{Mg} + \text{Fe}^{2+})$ ] be greater than 70, with the *mg* number

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samples (for example, see PRESNALL and HOOVER, 1984; Figure 5). However, even though fractionation drives residual liquids toward the quartz apex, Figure 5 of PRESNALL and HOOVER (1984) and Figure 1 show that primitive MORB glasses are not confined to or even concentrated in the quartz-poor portion of the MORB array. Although the number of primitive glass samples is limited, there is a suggestion of a concentration of compositions only slightly to the quartz-poor side of the *pl-hy* (Figure 1a) and *di-hy* (Figure 1b) joins, a position close to the location of a similar centrally located concentration of MORB compositions in general (WYLLIE *et al.*, 1981, Figure 3.3.34). (4) The distribution of primitive glass compositions does not follow the 1-bar boundary line along which olivine, plagioclase, and diopside crystallize, but the quartz-rich end of the distribution appears to be limited by this boundary line. This relationship is similar to that observed for MORB compositions in general (O'DONNELL and PRESNALL, 1980; GROVE and BRYAN, 1983; ELTHON and SCARFE, 1984).

#### EXPERIMENTAL DATA ON NATURAL COMPOSITIONS

One way of helping to clarify the origin of the primitive MORB glasses plotted in Figure 1 is to test the suitability of various experimentally produced basalts as parental liquids. We test suitability in two ways. The first method, which has been used

extensively by others (for example, STOLPER, 1980; ELTHON and SCARFE, 1984), is to note the relative positions of presumed parental and derived liquids on the triangular normative diagrams *ol-pl-q* and *ol-di-q* and determine visually if liquids thought to be derived are capable of being produced by crystal fractionation from liquids thought to be parental. For example, in the case of low-pressure crystallization of olivine from picritic liquids generated at high pressures, the test is accomplished simply by determining if the experimentally-produced picritic compositions lie along joins between primitive basalt compositions and the olivine apex. The second method involves a comparison of *mg* numbers and  $K_2O$ ,  $TiO_2$ , and  $Na_2O$  contents of the presumed parental and derived liquids. Fractional crystallization would decrease the *mg* number and increase the  $K_2O$ ,  $TiO_2$ , and  $Na_2O$  percentages in a derived liquid relative to these values in a parental liquid. The same changes would be produced by magma mixing between a parental liquid and another magma fractionated from an earlier similar parental liquid.

Application of the first method suggests that crystallization of olivine from experimentally produced picritic parental liquids (Figure 1) is capable of producing derivative liquids in the primitive MORB glass field, as pointed out by O'HARA (1968), GREEN *et al.* (1979), JQUES and GREEN (1980), STOLPER (1980), ELTHON and SCARFE

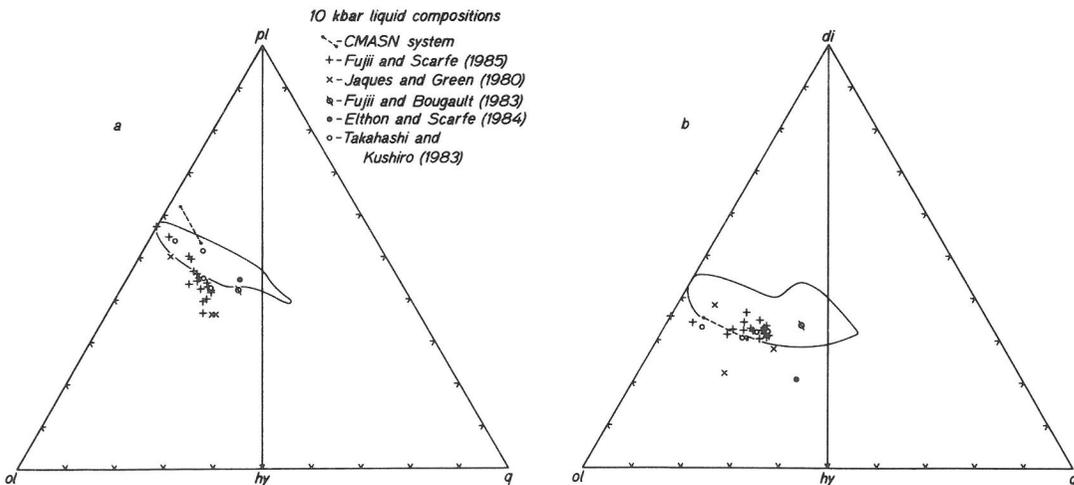


FIG. 2. Comparison of field of primitive MORB glasses (solid outline), 10 kbar liquids in the CMASN system (dashed line, taken from Figure 7), and 10 kbar liquids in equilibrium with olivine, orthopyroxene, and clinopyroxene in experiments on natural compositions. Positions of points are calculated in the same way as explained in the caption for Figure 1. In triangle *b*, the glass of JQUES and GREEN (1980) that meets our criteria for a parental magma is the point at 28 mol percent *di* and 25 mol percent *q* (see text).

(1984), and ELTHON (1985). On the other hand, Figure 2 shows that experimentally produced melts in equilibrium with olivine, orthopyroxene, and clinopyroxene at about 10 kbar lie near the olivine-rich border of the primitive MORB glass array. These 10 kbar liquids would be capable of producing compositions in most of the primitive MORB glass field by at most only a small amount of olivine crystallization (GREEN and RINGWOOD, 1967; KUSHIRO, 1973; PRESNALL *et al.*, 1979; FUJII and BOUGAULT, 1983; TAKAHASHI and KUSHIRO, 1983; PRESNALL and HOOVER, 1984, 1986; FUJII and SCARFE, 1985). Thus, application of the first method does not lead to a resolution of the controversy over the composition and depth of origin of primary magmas at spreading ridges; both scenarios are equally viable.

Now consider the second method. Small variations in  $\text{TiO}_2$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ , and  $mg$  number are generally of little consequence when the results of melting experiments on natural compositions are used for the usual purpose of showing approximate phase relationships. Typically, the phase relationships show a rough consistency and are useful even when one or more of these components do not correspond exactly to values found in rocks. In spite of this, if experimental data could be found that not only show appropriate phase relationships but also show consistent  $mg$  numbers and minor element concentrations, a higher level of confidence could be placed in the results. With this goal in mind, we have examined the available experimental melting data on natural compositions to see if any of the data meet these higher standards.

PRESNALL and HOOVER (1986) pointed out that  $mg = 67.7$  for the picritic liquid produced experimentally at 20 kbar by STOLPER (1980), is a value lower than that of any of the 40 primitive glasses. Also, at least one of the oxides,  $\text{K}_2\text{O}$ ,  $\text{TiO}_2$ , and  $\text{Na}_2\text{O}$ , has a smaller percentage in 39 of these glasses than in STOLPER's (1980) 20 kbar picritic liquid. Thus, Stolper's picritic liquid is not a suitable parental magma for these glasses. PRESNALL and HOOVER (1986) also pointed out that for the 20 and 25 kbar picritic liquids of ELTHON and SCARFE (1984), the amount of at least one of the oxides,  $\text{K}_2\text{O}$ ,  $\text{TiO}_2$ , and  $\text{Na}_2\text{O}$ , is higher than that of most of the primitive glasses. Thus, the picritic liquids of ELTHON and SCARFE (1984) are also unsuitable parental liquids for most of the primitive glasses.

We have carried out a more general review of experimental data on natural compositions to determine if picritic liquids produced experimentally by other investigators could be parental to the primitive MORB glasses even though these inves-

tigators may not have suggested that their picritic liquids are parental. Figure 3 shows that the picritic liquids of MYSEN and KUSHIRO (1977) are eliminated as parental magmas on the basis of their  $\text{K}_2\text{O}$  contents. Figure 4 shows that on the basis of their  $\text{TiO}_2$  contents, only a small proportion of the primitive glasses could be derived from picritic liquids reported by other investigators. Thus, if both the major and minor element concentrations of the liquids are considered, not just the positions of the liquids on triangular normative diagrams, none of the picritic liquids produced to date in laboratory experiments is a suitable parent for most of the primitive glasses.

The same criteria can be used to test possible parental liquids observed in laboratory experiments on natural compositions at lower pressures. Those advocating the generation of primary magmas in the vicinity of 10 kbar (for example, PRESNALL *et al.*, 1979) have argued that these primary magmas occasionally appear at the earth's surface either unmodified or only slightly changed in composition by such processes as fractional crystallization and magma mixing. Thus, we consider an experimentally produced liquid to be a suitable model of a

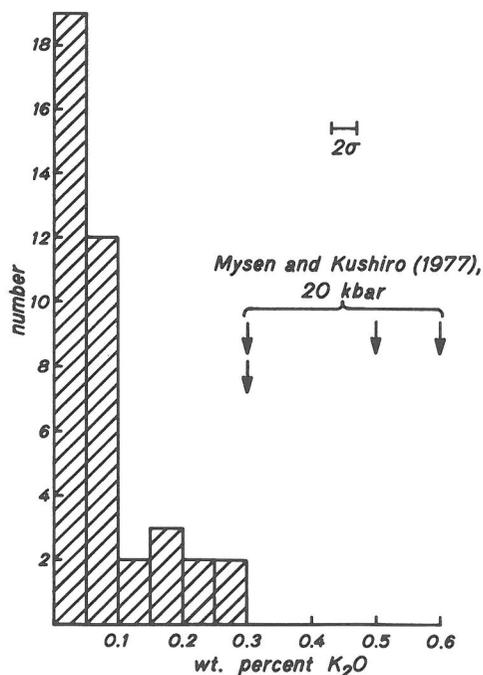


FIG. 3. Histogram of  $\text{K}_2\text{O}$  content of primitive MORB glasses (see Appendix 1, values normalized to a total analysis of 100 weight percent) and four picritic liquids produced experimentally by MYSEN and KUSHIRO (1977) at 20 kbar (arrows).

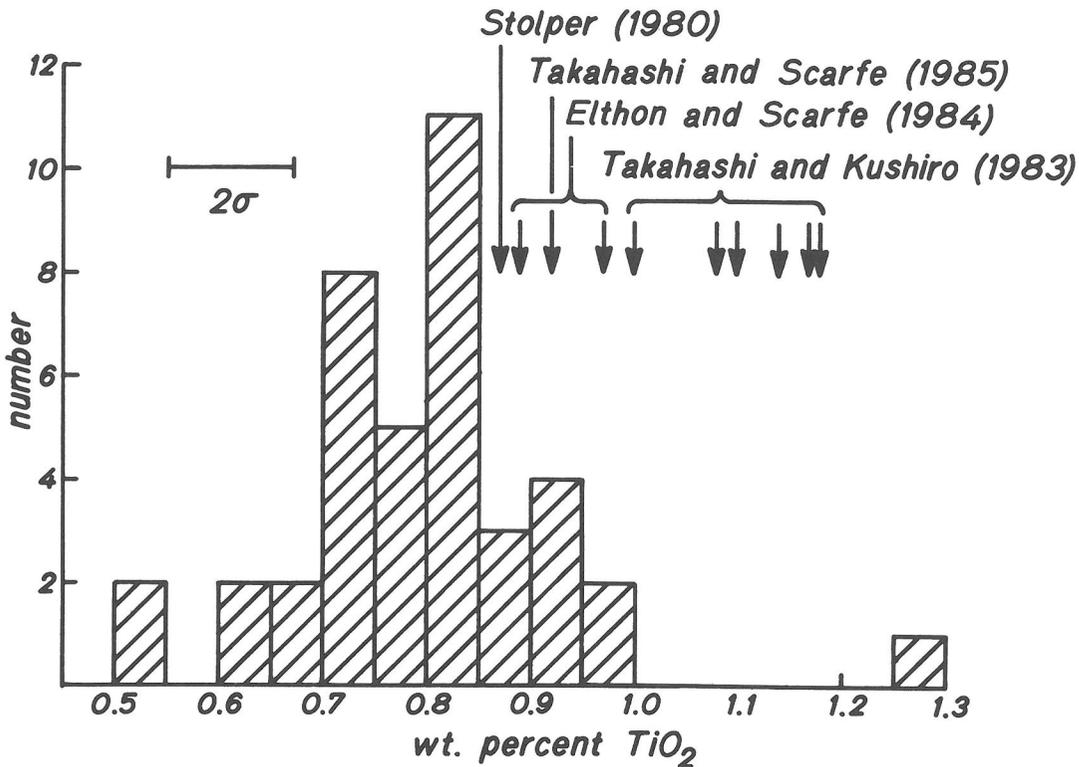


FIG. 4. Histogram of TiO<sub>2</sub> content of primitive MORB glasses (see Appendix 1, lower case values normalized to a total analysis of 100 weight percent) and picritic liquids produced experimentally at pressures from 20 to 35 kbar (arrows).

primary magma parental to the primitive glasses if its K<sub>2</sub>O, TiO<sub>2</sub>, and Na<sub>2</sub>O contents are either within or below the most commonly observed range of values for these oxides in the primitive MORB glasses. On the basis of Figures 3, 4, and 5, we require the K<sub>2</sub>O, TiO<sub>2</sub>, and Na<sub>2</sub>O contents to be less

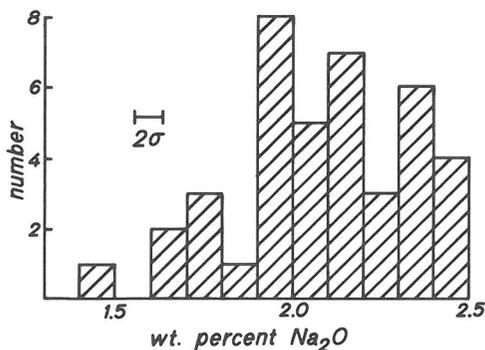


FIG. 5. Histogram of Na<sub>2</sub>O content of primitive MORB glasses (see Appendix 1, values normalized to a total analysis of 100 weight percent).

than 0.15 weight percent, 0.9 weight percent, and 2.4 weight percent, respectively. Also, we require the *mg* number to be greater than 70. Any liquid is considered that is in equilibrium with olivine, orthopyroxene, and clinopyroxene at pressures between 5 and 15 kbar. FUJII and KUSHIRO (1977) listed such a liquid composition with an *mg* number of only 64.4. Therefore, this liquid could not be a parental magma, a conclusion reinforced by its high TiO<sub>2</sub> (1.64 weight percent) and Na<sub>2</sub>O (2.70 weight percent) contents. TAKAHASHI and KUSHIRO (1983) listed 15 liquid compositions produced at pressures ranging from 5 to 15 kbar. All are eliminated as parental magmas by various combinations of high K<sub>2</sub>O, TiO<sub>2</sub>, and Na<sub>2</sub>O contents, and all except one are eliminated by their low *mg* numbers (<68.8). ELTHON and SCARFE (1984) listed two liquid compositions, one at 10 kbar and another at 15 kbar. The 10-kbar liquid composition is eliminated as a parental magma by its high TiO<sub>2</sub> content (1.4 weight percent) and low *mg* number (64.1). The liquid produced at 15 kbar is eliminated by its high TiO<sub>2</sub> content (1.18 weight percent).

Three studies gave liquid compositions that meet all the criteria for a parental basalt. FUJII and BOUGAULT (1983) gave one such analysis of a glass at 10 kbar (their Table 1, column 1). JAQUES and GREEN (1980) listed three liquid compositions produced by melting pyrolite, one each at 5, 10, and 15 kbar. The  $\text{TiO}_2$  (3.0–3.2 weight percent) and  $\text{Na}_2\text{O}$  (2.8–3.1 weight percent) contents of all three are too high for a parental magma. However, they also listed four liquids produced by melting Tinaquillo lherzolite, one each at 5 and 15 kbar and two at 10 kbar. The  $\text{K}_2\text{O}$  contents of the 15-kbar liquid and one of the 10-kbar liquids are too high (0.2 weight percent), but the remaining two liquids at 5 and 10 kbar could be parental (their Table 5, columns 7 and 11). FUJII and SCARFE (1985) listed 18 liquid compositions synthesized at 10 kbar. Five are eliminated as parental liquids by various combinations of high  $\text{K}_2\text{O}$ ,  $\text{TiO}_2$ , and  $\text{Na}_2\text{O}$  percentages, and the remaining thirteen meet our criteria for a parental magma for abyssal basalts. However, seven of these thirteen analyses have extremely high *mg* numbers of 78 to 82.1, with calculated coexisting olivine compositions of  $\text{Fo}_{92.2}$  to  $\text{Fo}_{94.1}$  (ROEDER and EMSLIE, 1970). If DICK and FISHER (1984) are correct that olivines from abyssal peridotites, which lie in the composition range  $\text{Fo}_{89}$ – $\text{Fo}_{91.6}$  (HAMLYN and BONATTI, 1980; DICK and FISHER, 1984), are residual compositions remaining from partial fusion of the mantle at spreading centers, the very high *mg* numbers of the seven glasses of FUJII and SCARFE (1985) are indeed unrealistic. Six of the glass compositions remain as suitable parental magmas produced at 10 kbar. The analyses are listed in columns 4 and 7 of Table 5 and columns 2, 7, 8, and 9 of Table 6 in FUJII and SCARFE (1985).

On the basis of the above strict criteria for a parental magma, only a few experiments on natural compositions have yielded suitable parental magmas at any pressure. These few experiments indicate that magmas generated at pressures from about 5 to 10 kbar are suitable parents for observed primitive MORB glasses. All of the 10-kbar liquids are plotted (among others) on Figure 2 and lie either close to or within the field of primitive MORB glasses. The 5-kbar liquid (not shown) lies slightly toward the olivine apex from the silica-rich end of the primitive MORB field. The lack of similar experimental support for picritic parental magmas generated at higher pressures does not necessarily indicate that such magmas cannot be primary; it may simply indicate that the proper experimental conditions have not yet been found. For example, suitable picritic compositions might occur if experiments were carried out at very high melting

percentages or on lherzolite starting materials low in  $\text{TiO}_2$ ,  $\text{Na}_2\text{O}$ , and  $\text{K}_2\text{O}$ . However, independent reasons would be needed for using starting compositions with reduced  $\text{TiO}_2$ ,  $\text{Na}_2\text{O}$ , and  $\text{K}_2\text{O}$  to avoid the criticism that the conclusions were defined by the initial conditions of the experiment.

Our emphasis on the importance of the *mg* number and the minor components  $\text{TiO}_2$ ,  $\text{Na}_2\text{O}$ , and  $\text{K}_2\text{O}$  might seem to be inconsistent with our use in the second part of the paper of phase relationships in the CMASN system, in which  $\text{FeO}$ ,  $\text{TiO}_2$ , and  $\text{K}_2\text{O}$  are not even present. No inconsistency exists, however, because the type of information obtained from the CMASN system (partial melt compositions as a function of pressure and percent melting) would be affected little by the inclusion of small amounts of additional components. For experiments on natural compositions, we use the *mg* number and the concentrations of  $\text{TiO}_2$ ,  $\text{Na}_2\text{O}$ , and  $\text{K}_2\text{O}$  to emphasize the fact that when the phase relationships (controlled mainly by the major elements), *mg* number, and certain minor elements are all considered, available experimental data on natural compositions are consistent only with the generation of non-picritic primary magmas at about 10 kbar. Scenarios involving picritic primary magmas must rely, at least at present, on supporting experimental data of a lower order of confidence in which the phase relationships are consistent but the *mg* number and certain minor element concentrations are not.

#### MELTING RELATIONSHIPS OF SIMPLIFIED LHERZOLITE IN THE SYSTEM $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-Na}_2\text{O}$

The solidus curve and liquid compositions along the solidus for simplified lherzolite in the 4-component system  $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$  (CMAS) have been determined by PRESNALL *et al.* (1979) over the pressure range of 1 bar to 20 kbar. We have extended this study by determining changes in the phase relationships for liquids containing up to 4 weight percent  $\text{Na}_2\text{O}$ . The data in the resulting 5-component system (CMASN) cannot be represented visually as a conventional phase diagram. However, the methods of PRESNALL (1986) can be used to calculate algebraically the solidus temperature, liquid path, crystal path, and phase proportions during partial fusion at each pressure for any arbitrarily chosen lherzolite composition within the 5-component system.

We present here preliminary results for equilibrium fusion of two model lherzolite compositions. The complete data set on which these calculated

Table 1. Mantle compositions

	Model Iherzolite A	Model Iherzolite B	Undepleted mantle (Carter, 1970)	Pyrolite 3 (Ringwood, 1975)
SiO <sub>2</sub>	46.7	46.2	42.9	46.1
TiO <sub>2</sub>	—	—	0.3	0.2
Al <sub>2</sub> O <sub>3</sub>	8.1	6.3	7.0	4.3
Fe <sub>2</sub> O <sub>3</sub>	—	—	0.4	—
FeO	—	—	9.0	8.2
MgO	39.3	43.1	35.1	37.6
CaO	5.3	4.1	4.4	3.1
Na <sub>2</sub> O	0.54	0.36	0.45	0.4

results are based will be presented elsewhere. Model Iherzolite composition A (Table 1) was calculated by mixing 70% of an assumed residue from partial fusion with 30% of our liquid composition in equilibrium with olivine, orthopyroxene, clinopyroxene, spinel, and plagioclase at 9.6 kbar in the CMASN system. Mineral proportions used for the residue are 74% olivine, 21% orthopyroxene, 4% clinopyroxene, and 0.5% spinel. These proportions are the same, within the stated uncertainties, as the average proportions of phases in residual periodotites from the ocean basins given by DICK and FISHER (1984). Mixing of 70% of this residue with 30% of the 9.6 kbar liquid composition yields a source mantle composition in which plagioclase, clinopyroxene, and spinel disappear nearly simultaneously from the crystalline assemblage during equilibrium partial melting at 9.6 kbar. This feature of the melting behavior is consistent with the observation of CARTER (1970) that clinopyroxene and spinel disappear from residual Iherzolite xenoliths from Kilbourne's Hole, New Mexico, at approximately the same forsterite content of coexisting olivine. The oxide percentages of the model Iherzolite A (Table 1) are similar to, but in all cases slightly higher than those of the corresponding oxides in the mantle compositions of CARTER (1970) and RINGWOOD (1975), a feature consistent with the absence of iron from the model composition (see Table 1).

Figures 6 and 7 show melting relationships for simplified Iherzolite composition A. The subsolidus phase assemblage at pressures less than 9.6 kbar is ol + en + di + pl (plagioclase Iherzolite) and at pressures above 10.8 kbar is ol + en + di + sp (spinel Iherzolite). Between 9.6 and 10.8 kbar, both plagioclase and spinel coexist with olivine, enstatite, and diopside just below the solidus. At pressures less than 9.6 kbar, the first crystalline phase to disappear during equilibrium melting is diopside, and it does so at liquid percentages ranging from 19 at 1 bar to 32 at 9.6 kbar. Exactly at 9.6 kbar, all five crystalline phases (olivine, orthopyroxene, clinopyroxene,

plagioclase, spinel) are retained until the amount of liquid reaches 32%, at which point plagioclase, diopside, and spinel disappear essentially simultaneously. Between 9.6 and 10.8 kbar, where the subsolidus assemblage ol + en + di + pl + sp exists, plagioclase is the first crystalline phase to be totally dissolved, and spinel follows at about 32% melting. From 10.8 to 20 kbar, spinel is the first crystalline phase to be totally dissolved, which occurs at melt percentages of about 32 at 10.8 kbar to about 30 at 20 kbar.

When the amount of liquid mixed with the assumed residue is changed from 30% to 20%, the composition of the model Iherzolite composition changes to that given in column 2 of Table 1 (composition B). In this composition, the concentrations of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CaO, and Na<sub>2</sub>O are closer to the compositions of CARTER (1970) and RINGWOOD (1975). If it is considered appropriate to combine molar MgO and FeO in the real mantle composition and treat this sum as comparable to molar MgO in the model mantle, composition B might then be a preferred model mantle composition. The melting

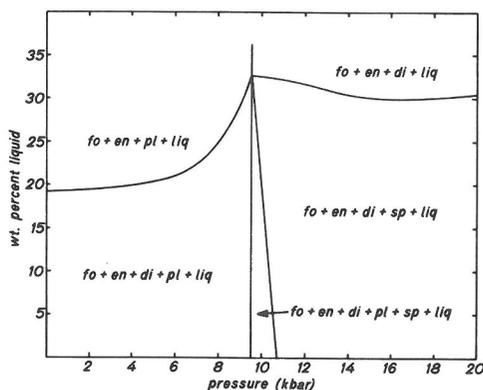


FIG. 6. Phase assemblages as a function of pressure and percent melting for simplified Iherzolite in the CMASN system.

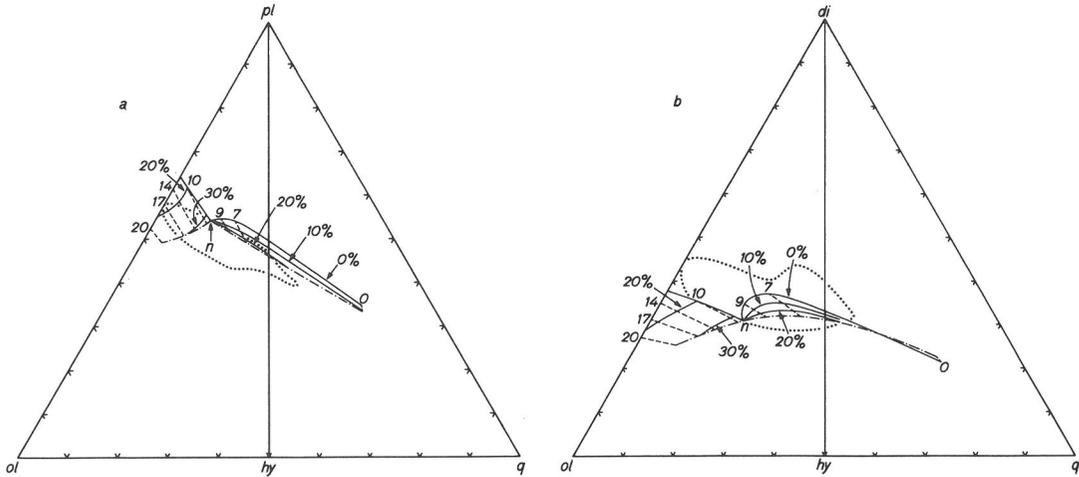


FIG. 7. Compositions of liquids as a function of pressure and weight percent melting for simplified lherzolite in the CMASN system. Solid lines are contours of constant liquid proportion. Dashed lines are isobars labeled according to their pressure in kbar. The dash-dot line shows the locus of points at which diopside disappears on melting at pressures below 9.6 kbar and the locus of points at which spinel disappears at pressures above 9.6 kbar. The dotted enclosure shows the field of primitive MORB glasses taken from Figure 1.

relationships for this composition would be similar to those shown in Figure 7 except that the 20% melting contour would be shifted approximately to the position of the 30% melting contour in Figure 7.

We have also calculated a model lherzolite on the assumption of 10% liquid mixed with the assumed residue. With this assumption, the  $\text{Na}_2\text{O}$  content of the model lherzolite is 0.19 weight percent, a value only about half that of the mantle compositions given by CARTER (1970) and RINGWOOD (1975). Thus, we consider this model composition to be unlikely.

#### EFFECT OF OTHER COMPONENTS ON MELTING RELATIONSHIPS IN THE SYSTEM $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-Na}_2\text{O}$

Before applying phase relationships in the CMASN system to the melting behavior of the mantle, we consider briefly the probable effect of additional components on the liquid compositions. Inclusion of iron oxide, the most important component missing from the CMASN system, would reduce liquidus temperatures for the olivine and pyroxene fields but would leave the plagioclase field relatively unaffected. Thus, in the *ol-pl-q* triangle (Figure 7a), boundary lines along which liquid compositions move during crystallization would be expected to move slightly away from the plagioclase apex, but in the *ol-di-q* triangle (Figure 7b), little change would occur.

Figure 2 shows a comparison between liquid compositions produced at 10 kbar in the CMASN system and those observed in melting experiments on natural compositions. All liquids are in equilibrium with olivine, orthopyroxene, and clinopyroxene and the CMASN liquids are also in equilibrium with spinel. As expected, liquid compositions in the melting experiments on natural compositions are shifted away from the plagioclase apex in Figure 2a relative to the CMASN liquids, but the two sets of data are essentially coincident in Figure 2b. This comparison supports the contention that missing components other than iron oxide have only a small effect on liquid compositions and that the CMASN phase relationships can be meaningfully applied to melting processes in the mantle if allowance is made for the slight shift in liquid compositions that would be produced by the addition of iron oxide. That is, liquid compositions in Figure 7a would shift slightly away from the *pl* apex but those in Figure 7b would remain approximately as shown.

#### VARIABLE VERSUS CONSTANT PRIMARY MAGMA COMPOSITIONS FROM THE MANTLE

YODER and TILLEY (1962) suggested that the mantle melts in a manner analogous to the formation of liquid at an isobaric invariant point. They pointed out that this type of melting behavior provides a mechanism for producing a uniform magma composition at a given pressure from a heteroge-

neous peridotite mantle in which the proportions of phases vary. Subsequently, PRESNALL (1969, 1979) showed that if melting occurs at an invariant point, not only can compositional heterogeneity of the source rock be tolerated without changing the initial melt composition, but a large amount of melt of constant composition can be produced. Of course, the mantle cannot melt at a true invariant point because the number of phases is small and the number of components is large. However, situations commonly exist with higher variance in which the melting behavior approximates that at an invariant point. That is, a relatively constant liquid composition can be derived from a somewhat heterogeneous source even when the amount of melting varies widely. In other situations with higher variance, changes in liquid composition with percent melting and with variations in the bulk composition of the source can be very large (PRESNALL, 1979). The problem reduces to a determination of the specific situation relevant to the mantle at various pressures. Several studies have addressed this issue for both natural compositions and simplified model systems but have not reached agreement (MYSEN and KUSHIRO, 1977; PRESNALL *et al.*, 1978, 1979; JAQUES and GREEN, 1980; STOLPER, 1980; TAKAHASHI and KUSHIRO, 1983; ELTHON and SCARFE, 1984; FUJII and SCARFE, 1985; KLEIN and LANGMUIR, 1986).

Melting relationships of model lherzolite A in the CMASN system (Figure 7) show that for pressures less than 9.6 kbar, the composition of the melt changes very little with percent melting up to the point of disappearance of the first crystalline phase, diopside. As pressure increases in the range 8 to 9.6 kbar, the magnitude of the change in composition for a given amount of fusion decreases and reaches zero at 9.6 kbar (point *n*). At this pressure, the melt composition remains fixed at *n* until the amount of liquid exceeds 32% (Figures 6 and 7). As pressure increases from 9.6 to 10.8 kbar (the pressure range in which plagioclase and spinel coexist in the simplified lherzolite just below the solidus), the melt composition remains fixed during isobaric melting until plagioclase disappears at melt percentages ranging from 32 at 9.6 kbar to zero at 10.8 kbar (Figure 6). Just as plagioclase completely dissolves, the liquid composition, shown in Figure 7, starts to move along the appropriate dashed isobaric line

(only the 10-kbar isobaric line is shown in this pressure interval), and it continues along this line until spinel is completely dissolved just as the liquid path reaches the dash-dot line at about 32% liquid. At pressures above 10.8 kbar, initial melt compositions are nepheline-normative (not shown in Figure 7), and as the percent liquid increases during isobaric equilibrium fusion, the liquid composition moves into the hypersthene-normative field (see GREEN and RINGWOOD, 1967, and TAKAHASHI and KUSHIRO, 1983, for similar results on natural compositions). A large amount of melting occurs prior to the disappearance of the first crystalline phase (spinel), but in this pressure range the change of liquid composition for a given amount of melting is much greater than it is at lower pressures.

These data indicate that generalizations applicable to all pressures cannot be made about the manner in which the mantle melts. At low pressures, especially near 9 to 10 kbar, the melting behavior approximates that at an invariant point; liquid is produced with a composition that changes only a small amount as a function of percent melting. At higher pressures, the liquid composition changes more rapidly as a function of percent melting. The transition between these two types of melting behavior occurs abruptly in a very narrow pressure interval between 9.6 and 10.8 kbar.

#### CONSTRAINTS ON PICRITIC PRIMARY MAGMAS

For model lherzolite A, the percent melting contours in Figure 7 show that if primary mid-ocean ridge basalts are produced by less than about 15% melting, picritic liquids with compositions lying toward olivine from the primitive MORB array do not exist at any pressure up to the 20-kbar limit of our data. Extrapolation of our data to higher pressures is straightforward up to about 22 kbar, the pressure of first appearance of garnet lherzolite along the solidus in the CMAS system (GASPARIK, 1984), and it is clear from Figure 7 that for this small additional extension of the pressure range, the constraint against picritic magmas at less than about 15% fusion of lherzolite A continues to hold. Compositions of liquids at higher pressures are more uncertain, but an indication of the changes to be expected is given by Figures 3.3.15 and 3.3.16 of WYLLIE *et al.* (1981). These diagrams show liquid compositions in equilibrium with simplified lherzolite in the CMAS system including a liquid at 40 kbar (DAVIS and SCHAIRER, 1965) that shows only a slight shift toward higher normative quartz<sup>4</sup> in comparison to the 22-kbar liquid.<sup>5</sup> This observa-

<sup>4</sup> See footnote 3.

<sup>5</sup> The estimated transition from spinel lherzolite to garnet lherzolite at the solidus was given in Figures 3.3.15 and 3.3.16 of WYLLIE *et al.* (1981) as 24 kbar rather than 22 kbar, as used here.

tion, coupled with the fact that the liquid at 15% fusion in the CMASN system lies deep within the alkalic (nepheline–normative) basalt field at 22 kbar, indicates that hypersthene–normative liquids at less than 15% fusion are unlikely to be produced from model lherzolite A at any pressure up to at least 40 kbar. If model lherzolite B is preferred, this conclusion would apply for amounts of fusion less than about 8%. Thus, although experimental confirmation of the phase relationships at high pressures is obviously important, present indications are that if primary magmas at spreading ridges are produced by less than about 8 to 15% fusion of the mantle source, these primary magmas are not picritic.

At 20 to 30% fusion of composition A (10 to 20% fusion for composition B), Figure 7 indicates that picritic liquids are possible if the pressure is higher than about 15 kbar. However, the composition range of these liquids is constrained to the quartz–poor portion of each triangle. Thus, low–pressure crystallization of olivine from picritic primary magmas produced by 10–30% fusion would be capable of yielding liquids in the quartz–poor end of the primitive MORB array but not in the quartz–rich end. This difficulty in producing primitive magma compositions in the quartz–rich end of the array would not be so constraining if an alternative mechanism could explain them. However, other mechanisms are not evident. As discussed below in the section on crystallization of primitive MORB glasses, primitive liquids near the quartz–rich end of the array could not be derived by fractional crystallization from primitive liquids near the quartz–poor end. Also, magma mixing with quartz–poor primitive liquids would be equally ineffective because the quartz–rich liquids would be one of the end members to be mixed.

The constraint against picritic primary magmas becomes less severe as the percent fusion increases, and olivine crystallization from picritic liquids might be capable of yielding the complete range of observed primitive liquids if the amount of fusion is allowed to range up to very high values considerably in excess of 30% for composition A or 20% for composition B. However, our data do not extend to these very high fusion percentages.

Because of the need for large amounts of fusion to produce picritic parental magma compositions, the amount of fusion responsible for the formation of mid–ocean ridge basalts is a critical parameter in determining the viability of picritic parental magmas. BENDER *et al.* (1978) estimated that basalts in the FAMOUS region were produced by about 20% melting of the mantle. For basalts in the Tamao region, BENDER *et al.* (1984) concluded that

about 5% melting was required. In a more recent evaluation of ridge basalts worldwide, KLEIN and LANGMUIR (1986) concluded from both major– and trace–element considerations that the average amount of fusion varies between about 8 and 22%. If these calculations of the amount of partial melting are correct, magma compositions only in the quartz–poor end of the primitive MORB array could be explained as derivatives from picritic parental magmas, and the origin of primitive mid–ocean ridge basalts by fractionation from picritic parental magmas fails as a general process.

#### GENERATION OF PRIMITIVE MORB GLASSES

When allowance is made for the effect of iron oxide on liquid compositions (Figure 2), it can be seen in Figure 7 that liquids produced in the pressure range of about 5 to 11 kbar would have compositions that lie near the olivine–rich margin of the primitive MORB glass array. As pressure decreases, the olivine field enlarges (KUSHIRO, 1968; PRESNALL *et al.*, 1978; O'DONNELL and PRESNALL, 1980, Figure 10), so primary magmas produced along the olivine–rich margin of the primitive MORB array would lie within the olivine field as they passed upward to the earth's surface. Thus, the phase relationships are consistent with a simple model for the origin of primitive MORB glasses that involves generation of non–picritic primary magmas over a range of pressures from about 5 to 11 kbar followed by a small amount of olivine crystallization at lower pressures. Alternatively, the primitive MORB liquids could be direct partial melts essentially unmodified by fractional crystallization. We feel that existing experimental data are not precise enough to distinguish between these two possibilities.

Previously, we argued that primary magmas at spreading ridges are generated at pressures from about 7 to 11 kbar (PRESNALL and HOOVER, 1984). We now believe the lower limit of this range must be decreased to about 5 kbar to account for the most silica–rich compositions in the primitive MORB array (Figure 7). The dashed isobars in Figure 7 show that variations in the amount of melting could contribute to the elongation of the primitive MORB array toward the quartz apex, but the elongation is much too large to be due mainly to this effect.

In the CMAS system, PRESNALL *et al.* (1979) emphasized the importance of a cusp on the mantle solidus at 9 kbar and argued that this cusp controlled the depth of generation and composition of primary

mid-ocean ridge basalts. PRESNALL *et al.* (1979, p. 26) suggested that for mantle peridotite, the cusp would appear as a low-temperature region spread over a small pressure interval. For the model mantle composition used here in the CMASN system, the cusp appears as a low-temperature region on the solidus that extends over the pressure interval 9.6 to 10.8 kbar. Comparison of Figures 1 and 7 shows that the greatest concentration of primitive MORB glass compositions lies close to liquid compositions in the CMASN system at about 9 to 10 kbar. Also, pressures at which the largest amounts of liquid are produced with the smallest changes in liquid composition with percent melting cluster around 9.6 kbar. Thus, our data in the CMASN system substantiate the main features of the model proposed earlier based on the CMAS system (PRESNALL *et al.*, 1979) and provide a more refined estimate of the range of pressures over which primary MORB magmas are generated.

#### CRYSTALLIZATION OF PRIMITIVE MORB GLASSES

The strong divergence of the quartz-poor end of the primitive MORB array from the 1-bar boundary along which olivine, plagioclase, and clinopyroxene crystallize (Figure 1) shows that the primitive MORB glasses have not resided in a crustal magma chamber long enough for their compositions to be controlled by crystal fractionation in that chamber. The compositional trend of the primitive MORB array conforms instead to the trend expected for primary magmas generated over the pressure interval of about 5 to 11 kbar with at most only slight modification by subsequent crystallization of olivine (Figure 7).

O'DONNELL and PRESNALL (1980) pointed out that a similar trend observed for more fractionated MORB glasses is not consistent with fractional crystallization of olivine, plagioclase, and clinopyroxene at any constant pressure but could be explained by *polybaric* crystallization of these phases as the magmas rise to the earth's surface. Therefore, it is important to examine the possibility that the quartz-poor end of the primitive MORB array may represent magmas that are parental to compositions in the quartz-rich end. Because all the primitive MORB glasses have very high *mg* numbers, such an explanation would require the decrease of *mg* number with increasing fractionation toward the quartz-rich end of the primitive MORB array to be extremely small. The experimental data of

WALKER *et al.* (1979), shown in Figure 8, demonstrate that for isobaric crystallization of olivine, plagioclase, and clinopyroxene, the change of *mg* number with percent normative quartz is, in fact, very large. Note also that the decreasing *mg* number with increasing normative quartz<sup>6</sup> is consistent with the decreasing forsterite content of coexisting olivine in their experiments. If the change of *mg* number for polybaric crystallization of these same phases is assumed to be similar, a magma at the quartz-rich end of the primitive MORB array with an *mg* number of 71 would require a parental magma at the quartz-poor end with an *mg* number of about 91, an obviously absurd result. We conclude that crystallization processes cannot explain the extension of the *primitive* MORB array toward the quartz apex. Because the phase relationships suggest that the compositions of primary magmas lie near the olivine-rich margin of the primitive MORB array, the primitive MORB glasses may in some cases be slightly modified by olivine crystallization. However, crystallization of olivine alone would move residual liquid compositions away from the olivine apex at a high angle to the long direction of the primitive MORB glass array. Thus, the possible existence of a small amount of olivine crystallization is consistent with our conclusion that the elongation of the primitive MORB array toward quartz is not due to crystallization processes.

Many authors have presented evidence for mul-

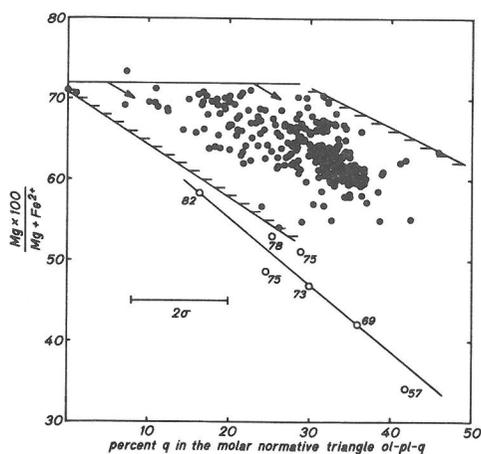


FIG. 8. Percent quartz in the molar normative triangle olivine-plagioclase-quartz as a function of *mg* numbers for FAMOUS and AMAR basalt glasses (filled circles, BRYAN and MOORE, 1977; BRYAN, 1983; STAKES *et al.*, 1984) and for basalt liquids in equilibrium with olivine, plagioclase, and diopside at 1 bar (open circles, WALKER *et al.*, 1979). Numbers beside the points of WALKER *et al.* are the forsterite contents of analyzed coexisting olivines.

<sup>6</sup> See footnote 3.

multiple parental magmas in the adjoining FAMOUS and AMAR areas of the Mid-Atlantic Ridge (BOUGAULT and HEKINIAN, 1974; BRYAN and THOMPSON, 1977; LANGMUIR *et al.*, 1977, BRYAN, 1979, 1983; LEROEX *et al.*, 1981; GROVE and BRYAN, 1983; STAKES *et al.*, 1984; PRESNALL and HOOVER, 1984). In Figure 8, glass compositions from the FAMOUS-AMAR area plot as a very wide band but with an overall slope close to that determined experimentally by WALKER *et al.* (1979). The correspondence of the two slopes indicates that crystallization processes were important in producing the less primitive FAMOUS-AMAR basalts. However, because of the great width of the FAMOUS-AMAR trend in Figure 8 and the existence of quartz-rich, very primitive glass compositions, crystallization from a single parental magma cannot explain the entire range of glass compositions. The broad trend is consistent, however, with the existence of multiple primary magmas of widely varying normative quartz content that crystallized olivine, clinopyroxene, and plagioclase under polybaric conditions as the magmas rose to the earth's surface. The arrows descending from the horizontal line in Figure 8 indicate expected crystallization trends from a range of primary magma compositions with *mg* numbers of about 70–73.

### CONCLUSIONS

Future detailed data from a wider range of ridge segments may reveal differences that obviate a uniform petrogenetic model applicable to all ridges, but data available at present show sufficient similarities that we believe the following generalizations are justified.

(1) Most mid-ocean ridge basalts are not derived from picritic primary magmas and none require a picritic parent.

(2) Primitive mid-ocean ridge basalts are best explained as products of at most only a small amount of olivine crystallization from multiple primary magmas. These primary magmas are not picritic and have a wide range of normative quartz content.<sup>7</sup>

(3) Phase relationships support the generation of primary magmas beneath spreading ridges over a pressure range of about 5 to 11 kbar, with the majority being generated at a low-temperature region on the solidus at about 9 to 10 kbar.

(4) Generation of multiple primary magmas over the pressure range of 5 to 11 kbar and polybaric

fractional crystallization both cause the normative compositions of MORB magmas to deviate in a similar way from the 1-bar boundary line along which olivine, plagioclase, and clinopyroxene crystallize.

(5) In agreement with many previous studies, we concur that data from the FAMOUS-AMAR area show that multiple parental magmas are capable of being produced in the same geographic area.

(6) The compositions of mid-ocean ridge basalts are best explained as the combined result of generation over a range of pressures followed by polybaric fractional crystallization as the primary magmas pass upward to the earth's surface. The fact that virtually the entire polybaric magma generation and crystallization process is recorded in the compositions of the lavas implies the existence of an eruptive mechanism capable of interrupting and sampling magmas at all depths and stages of evolution and bringing them rapidly to the earth's surface in a relatively unmodified condition. In such a model, magma mixing (DUNGAN *et al.*, 1978; DUNGAN and RHODES, 1978; RHODES *et al.*, 1979; WALKER *et al.*, 1979; STAKES *et al.*, 1984) would also be expected to occur during the sampling process. However, magma mixing, acting alone, could not explain the elongation of the primitive MORB array toward the quartz apex. Our model is at variance with certain aspects of some models (for example, PALLISTER and HOPSON, 1981; STAKES *et al.*, 1984) that emphasize an extended residence time and consequent fractional crystallization in a crustal magma chamber. We do not argue against the existence of a crustal magma chamber, but we believe that fractional crystallization in such a magma chamber is a subordinate process in the chemical evolution of magmas erupted at the earth's surface.

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Appendix 1. Primitive MORB glass compositions<sup>1</sup>

Sample No.	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub>	FeO <sup>2</sup>	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	Total	mg <sup>3</sup>	Reference
Atlantic Ocean														
519-4-1	49.07	0.74	16.44	0.03	8.86	0.16	10.15	11.65	2.13	0.07	n.d. <sup>4</sup>	99.30	70.4	BRYAN & MOORE (1977)
519-4-2	48.81	0.73	16.13	0.04	8.89	0.16	10.32	11.56	2.15	0.07	n.d.	98.86	70.6	BRYAN & MOORE (1977)
522-2-1	49.65	0.87	16.05	0.06	8.72	0.15	9.82	11.76	2.25	0.09	n.d.	99.42	70.0	BRYAN & MOORE (1977)
525-5-1	49.19	0.85	16.12	0.08	8.74	0.14	10.41	11.91	2.35	0.09	n.d.	99.88	71.2	BRYAN & MOORE (1977)
525-5-2	48.93	0.84	16.14	0.09	8.75	0.15	10.49	11.84	2.41	0.09	n.d.	99.73	71.3	BRYAN & MOORE (1977)
525-5-3	48.96	0.82	15.75	0.08	8.52	0.13	9.79	11.92	1.97	0.11	n.d.	98.05	70.4	BRYAN & MOORE (1977)
526-1-1B	51.36	0.78	15.03	0.11	7.86	0.10	9.01	12.38	2.04	0.10	n.d.	98.77	70.4	BRYAN & MOORE (1977)
527-1-2	49.50	0.66	16.51	0.11	8.76	0.17	9.86	12.68	2.08	0.04	n.d.	100.37	70.0	BRYAN & MOORE (1977)
528-4-1	49.93	0.72	15.82	0.08	8.37	0.15	9.78	12.67	1.96	0.05	n.d.	99.53	70.8	BRYAN & MOORE (1977)
529-3-2	50.82	0.92	15.92	0.06	7.91	0.13	9.38	12.07	2.30	0.16	n.d.	99.67	71.1	BRYAN & MOORE (1977)
530-3-1	49.98	0.77	15.24	0.00	8.60	0.13	10.11	12.45	2.23	0.07	n.d.	99.58	70.9	BRYAN & MOORE (1977)
534-2-1	50.30	0.84	15.99	0.08	8.70	0.13	9.91	12.33	2.16	0.09	n.d.	100.53	70.2	BRYAN & MOORE (1977)
534-2-2A	50.37	0.84	15.86	0.09	8.57	0.16	9.82	12.33	2.18	0.09	n.d.	100.31	70.4	BRYAN & MOORE (1977)
ARP-73-10-3	50.6	1.05	15.0	0.00	8.97	0.18	8.70	12.5	2.43	0.11	n.d.	99.54	73.4	BRYAN (1979)
AII-77-76-61	51.2	0.84	15.0	0.08	7.98	0.16	9.02	13.3	1.89	0.08	n.d.	99.55	70.1	BRYAN (1979)
AII-77-76-71	51.4	0.83	15.0	0.07	8.05	0.16	9.15	13.2	1.97	0.09	n.d.	99.92	70.2	BRYAN (1979)

ARP-74-14-31	48.2	0.51	17.0	n.d.	8.51	0.16	10.1	12.7	2.34	0.04	n.d.	99.56	71.1	BRYAN (1979)
ARP-74-14-33	48.2	0.50	16.9	0.01	8.50	0.15	9.91	12.8	2.30	0.04	n.d.	99.31	70.7	BRYAN (1979)
3-14-10-1 <sup>5</sup>	50.0	0.79	17.4	n.d.	8.22	0.13	9.81	12.9	2.28	0.02	n.d.	101.55	71.2	FREY <i>et al.</i> (1974)
3-18-7-1,1 <sup>5</sup>	50.3	0.73	16.6	n.d.	7.99	0.12	10.2	13.2	2.00	0.01	n.d.	101.15	72.6	FREY <i>et al.</i> (1974)
3-18-7-1,4	50.4	0.79	17.1	n.d.	7.97	n.d.	9.88	12.9	1.62	0.02	n.d.	100.68	72.0	FREY <i>et al.</i> (1974)
A27-99S1	49.86	0.71	16.93	n.d.	8.12	n.d.	9.49	13.16	1.71	0.02	0.04	100.04	70.8	MELSON <i>et al.</i> (1976a)
A42-96N1	50.57	0.92	15.62	n.d.	7.96	n.d.	9.21	13.32	1.99	0.26	0.10	99.95	70.6	MELSON <i>et al.</i> (1976a)
72-17-44	49.68	0.86	16.75	n.d.	7.67	0.13	9.19	12.23	2.31	0.05	0.10	98.97	71.3	O'DONNELL & PRESNELL (1980)
TR-154-14-D1	51.36	1.29	16.48	n.d.	7.21	0.06	8.39	12.02	2.49	0.25	0.09	99.64	70.7	SIGURDSSON (1981)
ARP-74-10-16 <sup>6</sup>	49.47	0.82	15.23	0.09	8.15	0.14	10.66	12.21	1.94	0.16	0.10	98.97	73.1	FUJII & BOUGAULT (1983)
CYP-31-35 <sup>7</sup>	49.57	0.85	15.26	0.09	8.28	0.14	10.63	12.11	2.11	0.19	0.11	99.34	72.7	FUJII & BOUGAULT (1983)
VG-202	50.73	0.92	15.61	n.d.	7.97	n.d.	9.34	13.29	1.94	0.24	0.10	100.14	70.8	MELSON <i>et al.</i> (1976b)
VG-203	50.41	0.92	15.64	n.d.	7.95	n.d.	9.09	13.35	2.05	0.28	0.11	99.80	70.3	MELSON <i>et al.</i> (1976b)
VG-297	50.14	0.74	16.81	n.d.	8.25	n.d.	9.59	13.01	1.71	0.04	0.04	100.33	70.7	MELSON <i>et al.</i> (1976b)
VG-416	50.73	0.73	16.88	n.d.	8.22	n.d.	9.84	13.33	1.68	0.04	0.05	101.50	71.3	MELSON <i>et al.</i> (1976b)
VG-607	49.97	0.73	17.26	n.d.	8.39	n.d.	9.51	12.92	1.99	0.01	0.03	100.81	70.1	MELSON <i>et al.</i> (1976b)
VG-611	49.95	0.69	17.29	n.d.	7.91	n.d.	9.14	13.23	1.76	0.00	0.04	100.01	70.5	MELSON <i>et al.</i> (1976b)
Indian Ocean														
VG-649	50.41	0.92	15.64	n.d.	7.95	n.d.	9.09	13.35	2.05	0.28	0.11	99.80	70.3	MELSON <i>et al.</i> (1976b)
Pacific Ocean														
F	49.15	0.96	17.58	n.d.	8.01	n.d.	9.58	12.14	2.38	0.04	0.10	99.94	71.2	NATLAND & MELSON (1980)
H	49.21	0.97	17.54	n.d.	7.97	n.d.	9.12	12.35	2.43	0.04	0.09	99.72	70.3	NATLAND & MELSON (1980)
1561-1622	48.47	0.88	17.39	0.04	8.03	0.16	9.83	12.26	2.47	0.03	n.d.	99.56	71.7	PERFIT <i>et al.</i> (1985) <sup>8</sup>
F2-1	49.85	0.86	17.51	0.05	8.12	0.21	9.80	12.92	2.15	0.02	n.d.	101.49	71.4	PERFIT <i>et al.</i> (1985) <sup>8</sup>
F3-2	49.46	0.83	17.42	0.04	8.11	0.14	9.85	12.72	2.14	0.04	n.d.	100.75	71.6	PERFIT <i>et al.</i> (1985) <sup>8</sup>
F1 <sup>9</sup>	47.2	0.77	16.9	0.07	8.80	0.14	10.90	12.2	2.05	0.02	n.d.	99.05	72.0	PERFIT <i>et al.</i> (1985) <sup>8</sup>

<sup>1</sup> All analyses by electron microprobe except as indicated.

<sup>2</sup> Total Fe as FeO.

<sup>3</sup>  $mg = 100 \text{ Mg}/(\text{Mg} + \text{Fe}^{2+})$  when  $\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$  is assigned the value 0.86 (PRESNALL *et al.*, 1979).

<sup>4</sup> n.d. = not determined.

<sup>5</sup> FREY *et al.* (1974) also list trace element concentrations.

<sup>6</sup> X-ray fluorescence analysis. Sample also contains 247 ppm Ni.

<sup>7</sup> X-ray fluorescence analysis. Sample also contains 255 ppm Ni, 0.52 ppm Ta, 1.32 ppm Hf, and 0.42 ppm Tb.

<sup>8</sup> Also M. R. PERFIT (personal communication, 1985).

<sup>9</sup> Direct current plasma analysis by C. H. LANGMUIR (M. R. PERFIT, personal communication, 1985).

