

Magma density at high pressure Part 2: A test of the olivine flotation hypothesis

CLAUDE T. HERZBERG

Department of Geological Sciences, Rutgers University, New Brunswick, New Jersey, 08903 U.S.A.

Abstract—An algorithm is presented for computing the density of any complex magma composition to pressures in the 15–20 GPa range. It is based on an estimation of the bulk modulus of the magma from the bulk moduli of its constituent oxide components, mixed in proportion to their volume fractions according to the Voigt-Reuss-Hill approximation. An examination is made of the effects of the contradictory elastic parameters reported in Part 1 (HERZBERG, this volume), and a test is made of the hypothesis that olivine may become less dense than naturally occurring magmas at some finite depth in the upper mantle (STOLPER *et al.*, 1981).

Two elastic models are considered. In the first, silicate liquids compress according to the law of corresponding states; the effect of composition on the compressibility of the melt is large, and the composition of the melt phase must be specified. In the second, silicate liquids compress in violation of the law of corresponding states, and all magma compositions compress by similar amounts over any given increment of pressure.

It is demonstrated that the olivine flotation hypothesis is unconvincing for silicate liquids which compress in observation of the law of corresponding states. Although an olivine-liquid density crossover is invariably computed, it is located at pressures where equilibrium between the two phases is an assumption which is either in doubt or demonstrably in error. For a liquid lherzolite composition, the density is calculated to be the same as the density of olivine at about 15 ± 2 GPa. However, this is likely to be an “apparent” olivine-liquid density crossover rather than a real one because it is within this pressure range where olivine and liquid lherzolite become unstable; olivine is replaced by majorite as the stable liquidus phase, and olivine is transformed to its high density modified spinel polymorph. For a high Mg komatiite composition, the density is also calculated to be the same as that for olivine at about 15 GPa. However, this density comparison is unambiguously erroneous because olivine is not in equilibrium with komatiite at 15 GPa; olivine is replaced by garnet as the liquidus phase in the 6 to 7 GPa range, and, again, the modified spinel polymorph of olivine is likely to be stable at about 15 GPa.

The olivine flotation hypothesis is supported for silicate liquids which compress in violation of the law of corresponding states. For komatiite and lherzolite liquids, this elastic law predicts that a real olivine-liquid density crossover will exist in the 5 to 6 GPa range.

The predicted pressures of the real and apparent density crossover points are so different for each elastic model, that one or the other should be easily falsifiable by experimentation. Presently available constraints from shock wave and Stokes' Law experiments are most consistent with liquids which compress in observation of the law of corresponding states.

INTRODUCTION

IN PART 1 of this paper (HERZBERG, 1987) it was demonstrated that the available information on the compressibility characteristics of silicate liquids is contradictory. Silicate liquids either do or do not compress in observation of the empirical law of corresponding states (HERZBERG, 1987). If the law is obeyed, the effect of composition on the compressibility of the melt is significant. If it is not obeyed, then all silicate melts will compress by the same amount over any specified increment of pressure.

The consequences of these two contradictory possibilities on the density of magmas at high pressures are profoundly different, and is the subject of this paper. With constraints now available on the partial molar volumes, thermal expansion coefficients, and bulk moduli of the oxide components,

it is possible, at least in principle, to calculate the density of any magma at any temperature and pressure of the geologist's choice. However, in practice there remains a number of ambiguities, the most serious of which was discussed in Part 1 (HERZBERG, 1987). That is, even if all the elastic parameters for the oxide components were unambiguously known, there is some uncertainty as to how they should be mixed to yield the desired result, this being the bulk modulus of a complex magma. The algorithm chosen is the Voigt-Reuss-Hill mixing scheme because it seems to work best for a number of alkali oxide-SiO₂ binary systems; it will be shown here that it also seems to work for complex magma compositions.

Two other important problems are encountered in any attempt to calculate the density of magmas at high pressures. These are: 1) the extent to which

ideal mixing holds, and 2) the role of structural changes in the melt (*e.g.*, possible coordination changes of individual cations). In the calculations which follow it is assumed that the oxide components mix ideally with respect to volume, and that pressure-induced structural rearrangements will not significantly increase the density of natural ultrabasic magmas at high pressures. The former assumption seems relatively successful in the work of BOTTINGA and WEILL (1970) and NELSON and CARMICHAEL (1979), and was adopted in Part 1 of this paper. The latter assumption is certainly contentious for aluminous compositions such as albite and jadeite (*e.g.*, BOETTCHER *et al.*, 1982; OHTANI *et al.*, 1985; FLEET *et al.*, 1984). However, natural magmas generated by anhydrous melting in the mantle at high pressures are ultrabasic in composition, not basaltic (HERZBERG, 1983; TAKAHASHI and SCARFE, 1985), and their alumina contents are fairly low; consequently even if structural changes do occur in the 10 to 20 GPa pressure range the effect will probably be small.

In view of these difficulties, the density of magmas at high pressures estimated by calculation rather than by direct experimental determination are subject to important uncertainties. Accordingly, the approach taken here has been to adopt the Voigt-Reuss-Hill mixing algorithm in which the contradictory elastic parameters discussed in Part 1 (HERZBERG, 1987) are incorporated. This method is then tested by making predictions of the high pressure densities of several complex silicate melts for which independent constraints are available. Finally, an examination is made of the hypothesis that there exists a finite depth in the upper mantle below which natural magmas may be denser than coexisting olivine crystals (STOLPER *et al.*, 1981).

METHOD OF CALCULATION

For component *i* of interest its partial molar volume, \bar{V}_i^0 , at 1400°C, thermal expansivity, α_i , and isothermal bulk modulus at 1 atmosphere, K_i^0 , are listed in Table 1. The partial molar volumes and thermal expansivities are the model parameters developed in Part 1 (HERZBERG, 1987). The bulk moduli are valid for liquids which observe and violate the law of corresponding states.

At 1 atmosphere and temperature *T* the partial molar volume of *i* is \bar{V}_i and is determined from:

$$\bar{V}_i = \bar{V}_i^0 + \alpha_i(T - 1400) \quad (1)$$

where *T* is in °C. The molar volume *V* is simply:

$$V = \sum X_i \bar{V}_i. \quad (2)$$

The density at temperature *T* and 1 atmosphere is ρ' and becomes:

$$\rho' = \sum X_i M_i / V \quad (2)$$

where M_i is the gram formula weight of *i*. At *T* and pressure of interest *P*, density ρ and pressure are related by a Birch-Murnaghan equation of state (BIRCH, 1952; STOLPER *et al.*, 1981; equation (6), HERZBERG, 1987).

HERZBERG (1987) suggested that $K' = dK^0/dP$ is close to 4 for liquid Mg_2SiO_4 and Fe_2SiO_4 . This value is similar to that proposed by RIGDEN *et al.* (1984) for liquid $An_{36}Di_{64}$ (mol percent) and many crystalline compounds as well (ANDERSON, 1972). Accordingly, the value used throughout these calculations is 4.

The isothermal bulk modulus of a complex liquid composition at 1 atmosphere is evaluated from the bulk moduli of its end-members using the Voigt-Reuss-Hill relation:

$$K^0 = [\sum V_i K_i^0 + (\sum (V_i / K_i^0))^{-1}] / 2 \quad (4)$$

Table 1. Volume and elastic parameters of oxide components in silicate liquids at 1400°C

	V_i^0 (cm ³ /gfw)	K_i^0 (GPa)	$(\alpha_i \times 10^5 / ^\circ\text{C})$
SiO ₂	27.08 (0.19)	13.0 (1.3)	1.1
Al ₂ O ₃	36.83 (0.47)	20.9 (4.5)	6.2
FeO	13.31 (0.38)	73.6 (61.6–85.9) O 28.7 (4.5) V	23.6
MgO	11.87 (0.37)	84.8 (70.9–99.1) O 38.6 (6.1) V	23.4
CaO	16.49 (0.28)	56.6 (47.4–65.7) O 49.4 (5.4) V	24.3
Na ₂ O	28.82 (0.22)	14.1 (8.0–19.9)	24.7
K ₂ O	46.05 (0.39)	8.0 (3.9–11.3)	26.1

O = law of corresponding states observed.

V = law of corresponding states violated.

Uncertainties are indicated in parentheses as \pm from the mean, or a range about the mean.

where V_i is the volume fraction of i in the melt phase, and K_i are listed in Table 1. The temperature derivative of the bulk modulus dK^0/dT is small and was thus set at zero. Consequently, at 1 atmosphere the bulk modulus of component, i , at temperature, T , (i.e., K) is the same as the bulk modulus at the 1400°C reference temperature (i.e., K^0). The volume fraction of i can be evaluated from:

$$V_i = X_i \bar{V}_i / V. \quad (5)$$

A computer program in BASIC which calculates the density of a magma according to the above algorithm is given in Appendix I.

TESTS OF THE MODELS

Shock wave studies on molten material having the composition $An_{36}Di_{64}$ have been obtained by RIGDEN *et al.* (1984), and these results are compared with the calculated densities (Figure 1). The experimental densities are those along an adiabat having an initial temperature of 1400°C at 1 atmosphere. The data point at 23.54 GPa is probably a minimum bound due to the effects of shock heating at pressures greater than 10 GPa (RIGDEN *et al.*, 1984). From these Hugoniot data an isentropic bulk modulus of $22.6 \pm .8$ GPa and a pressure derivative $dK_s/dP = 4.15$ were obtained (RIGDEN *et al.*, 1984). For liquids which observe the law of corresponding states, the isothermal bulk modulus is calculated to be 22.8 ± 3.3 GPa at 1400°C. The calculated pres-

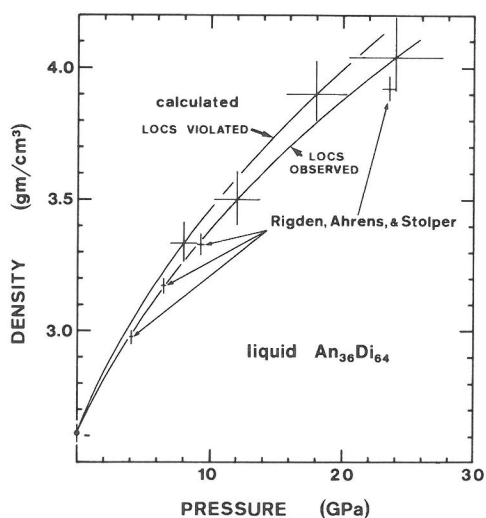


FIG. 1. Density of liquid $An_{36}Di_{64}$ (mol percent) calculated at 1400°C using elastic parameters with the "Law Of Corresponding States" (LOCS) observed and violated, and shock wave data from RIGDEN *et al.* (1984).

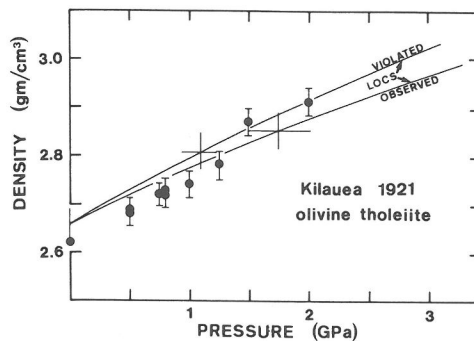


FIG. 2. Density of Kilauea 1921 olivine tholeiite calculated at 1400°C using elastic parameters with the "Law Of Corresponding States" (LOCS) observed and violated, and falling sphere data of FUJII and KUSHIRO (1977) and FUJII (1978).

sure-density relations shown are, therefore, in excellent agreement with the shock wave data. Differences in density stemming from the isothermal versus isentropic cases are small.

The amount of shock heating required to fit the 23.54 GPa point has been calculated by simply increasing the temperature of calculation until the density is sufficiently reduced so as to match the experimental data. The temperature is about 1700°C; given the adiabatic character of these data a temperature increase of no more than 300°C is indicated in these experiments.

The isothermal bulk modulus calculated for the liquid that violates the law of corresponding states is 20.0 ± 2.5 GPa, and the pressure-density relations are shown also in Figure 1. Although the fit to the experimental data is not as good, there is a slight overlap in the error bars between the calculated and experimentally observed densities.

The densities of liquid olivine tholeiite having the composition of Kilauea 1921 have been determined experimentally (FUJII and KUSHIRO, 1977; FUJII, 1978; Figure 2), and are compared with calculated values. If this liquid observes the law of corresponding states, its isothermal bulk modulus is calculated to be 21.8 ± 3.4 GPa. In all cases the error bars from the calculated and experimentally observed densities overlap. However, it can be seen that the experimental densities at pressures less than about 1.2 GPa are consistently lower than the calculated ones, and at higher pressures the reverse is true. Indeed, there appears to be a discontinuous change in the experimentally determined pressure-density relations at about 1.2 GPa, an observation which is consistent with a change in melt structure at that pressure. However, other falling sphere ex-

periments on a range of basaltic compositions similar to Kilauea 1921 do not show this feature (KUSHIRO, 1982).

For Kilauea 1921 which violates the law of corresponding states, K^0 is 18.1 ± 2.6 GPa. The calculated densities at 1.5 and 2.0 GPa are in better agreement with the experimental data; however, for the lower pressure data in the 0.5 to 1.2 GPa range, the agreement is poor.

Recent olivine flotation and settling experiments have been carried out with pure forsterite crystals and a basalt compositionally similar to Kilauea 1921 (T. FUJII, personal communication). The results are shown in Figure 3. Elastic parameters for forsterite and the temperature and pressure derivatives are taken from Part 1 (HERZBERG, 1987). Although reaction rims surrounding the forsterite crystals demonstrate unambiguously that this is not an equilibrium crystal-liquid pair, the well-bracketed settling and flotation experiments place important constraints on the contradictory elastic models. Densities calculated with the law of corresponding states observed are in excellent agreement with the experimental data which demonstrate forsterite settling at 6.5 GPa and flotation at 8.5 GPa; neutral buoyancy is calculated at 7.5 GPa. However, densities calculated in violation of the law of corresponding states seriously conflict with the experimental observations. Whereas forsterite flotation is predicted at 6.5 GPa, it has been observed to settle (T. FUJII, personal communication).

THE EFFECT OF TEMPERATURE, PRESSURE, AND COMPOSITION ON OLIVINE-MAGMA DENSITY RELATIONS

Olivine flotation has now been demonstrated in two separate sets of experiments. The first was the observation of flotation at atmospheric pressure for intermediate bulk compositions on the join Mg_2SiO_4 - Fe_2SiO_4 (HERZBERG *et al.*, 1982), and was explained by the extreme partitioning of the heavy element Fe into the melt phase. Secondly, as noted above, forsterite has been observed to float in a tholeiitic liquid composition at high pressures (T. FUJII, personal communication). Although useful information is obtained on the elastic properties of such melt compositions, the observation of forsterite flotation has geological limitations because forsterite and tholeiite are not in equilibrium under the experimental conditions. Indeed, there exist a wide range of temperatures, pressures, and compositions wherein olivine is calculated to float in magmatic liquids, and these are illustrated in this section. The geological restrictions to these conditions will be discussed in the following section.

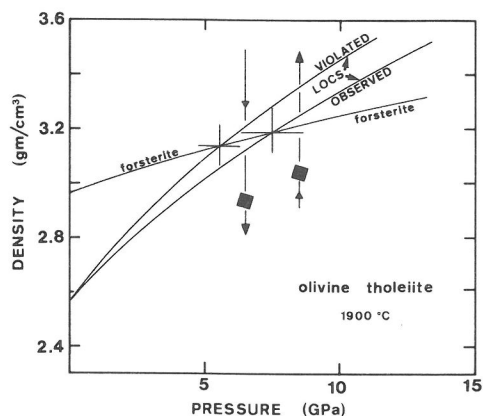


FIG. 3. Densities of pure forsterite and Kilauea 1921 olivine tholeiite calculated with the Law of Corresponding States (LOCS) observed and violated compared with forsterite settling and flotation experimental data (T. FUJII, personal communication). Arrows indicate olivine flotation (up) and settling (down).

The effects of temperature, pressure, and composition on olivine-magma density relations are explored systematically and in isolation from each other in Figures 4 and 5. The densities of crystalline olivines having the compositions FO_{80} , FO_{90} , and FO_{100} have been determined by a linear interpolation of the elastic parameters of pure forsterite and fayalite reviewed in Part 1 (SUZUKI *et al.*, 1981; 1983; SUMINO, 1979; KUMAZAWA and ANDERSON, 1969). This interpolation is justified because the elastic properties of the end-members are so similar. Additionally, volumes at 1 atmosphere and 25°C were obtained from the work of FISHER AND MEDARIS (1969). The algorithm used is listed in Appendix II as a computer program in BASIC. It should be noted that olivine densities so obtained are similar to those calculated from the equation offered by HAZEN (1977), but are about 0.05 gm/cm³ higher at 5 GPa, and 0.1 gm/cm³ lower at 17 GPa. The method chosen here is considered to be superior because d^2P/dP^2 is negative, whereas it is positive in the HAZEN algorithm.

Isothermal density relations at 1400°, 1800°, and 2200°C for two melt compositions which compress in conformity with the law of corresponding states are illustrated in Figures 4A-C. The case for liquids which compress in violation of this law is shown in Figures 5A-C. Two very different melt compositions were selected. These are average mid ocean ridge basalt (MORB; MELSON *et al.*, 1976), and a melt having the composition of fertile garnet lherzolite PHN 1611 (NIXON and BOYD, 1973); both are listed in Table 2.

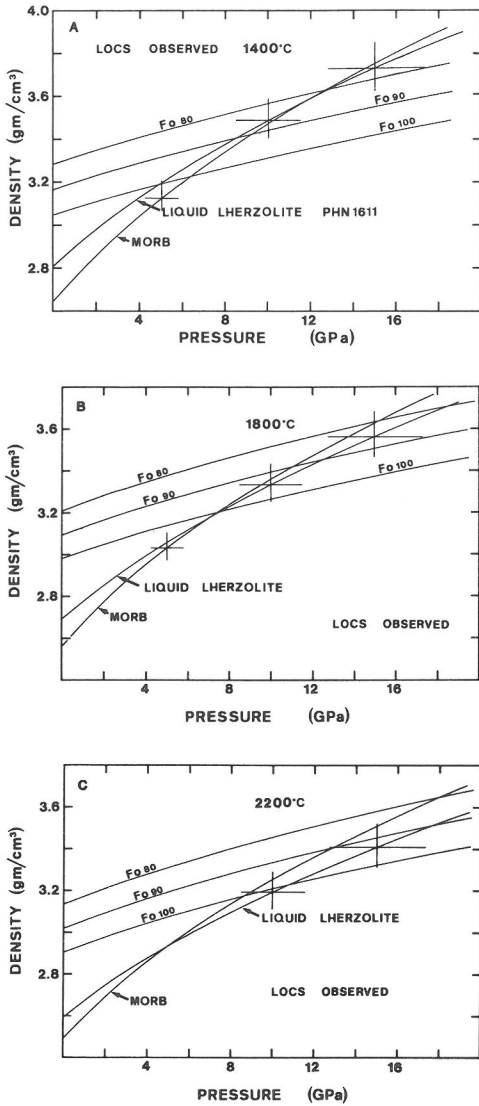


FIG. 4. Densities of MORB tholeiite and liquid lherzolite PHN 1611 which observe the Law Of Corresponding States (LOCS) compared to various olivine compositions at 1400°C (4A), 1800°C (4b), and 2200°C (4C). Note that MORB liquids become denser than liquid lherzolite at high pressures.

At any temperature the density of MORB is less than that for the liquid lherzolite at low pressures. However, at high pressures MORB becomes denser than liquid lherzolite when the law of corresponding states is observed (Figure 4). This arises from the effect of composition on the bulk modulus. Where the law of corresponding states is violated, there is no compositional effect (Figures 5A-C), and the density-pressure curves for each composition become semiparallel.

At 1400°C the olivine-melt density crossover is located at 4 to 6 GPa for both liquid compositions and pure Fo_{100} (Figure 4A). With increasing Fe content in the olivine crystals, the crossover shifts to progressively higher pressures, becoming 13 GPa for Fo_{80} . Because olivines crystallizing from lherzolite liquids are more forsterite-rich than those which crystallize from tholeiites, it is clear that the composition of olivine must be specified in any examination of olivine-liquid density comparisons.

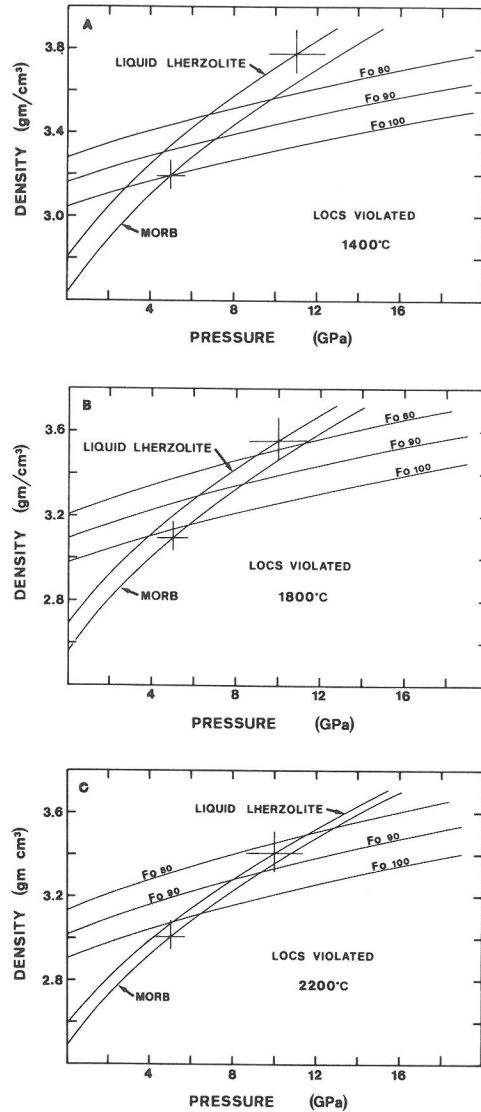


FIG. 5. Densities of MORB tholeiite and liquid lherzolite PHN 1611 which violate the Law Of Corresponding States (LOCS) compared to various olivine compositions at 1400°C (5A), 1800°C (5B) and 2200°C (5C). Note that liquid lherzolite remains denser than MORB at all pressures.

Table 2. Selected magma compositions (weight percent) for density calculations

	Basalt	Komatiite	Liquid lherzolite
SiO ₂	50.53	45.23	43.70
Al ₂ O ₃	15.27	6.17	2.75
FeO	10.46	11.48	10.05
MgO	7.47	28.59	37.22
CaO	11.49	5.89	3.26
Na ₂ O	2.62	0.60	0.33
K ₂ O	0.16	0.04	0.14
K (GPa)	O 21.1 (3.2) V 18.0 (2.6)	27.7 (4.2) 19.9 (2.7)	30.1 (4.5) 20.5 (2.8)

All Fe₂O₃ where reported is converted to FeO.

Data sources: Basalt, MELSON *et al.* (1976); Komatiite, NESBITT and SUN (1976); Lherzolite is PHN 1611, NIXON and BOYD (1973).

O = law of corresponding states observed.

V = law of corresponding states violated.

Values of *K* are valid at 1400°C; these become reduced at higher temperatures due to changes in the volume fractions of the oxide components, taking the appearance of a temperature derivative; estimated uncertainties are given in parentheses.

Furthermore, the comparisons shown in Figure 4A are rather meaningless because it is well established that neither tholeiite nor liquid lherzolite can be generated at an anhydrous mantle at temperature as low as 1400°C in the pressure range where a density crossover is presumed to occur (see next section). At 1800°C and 2200°C all crossover pressures are located at higher pressures. This result arises from thermal expansivity differences between the olivine and melt phases. Indeed, whereas attention has been repeatedly focused on the consequences of the high compressibility of silicate liquids compared to olivine (*e.g.*, STOLPER *et al.*, 1981), the fact that these liquids have a thermal expansion coefficient which is about 3 times higher than crystalline silicates has been largely ignored. It is the tradeoff between liquid thermal expansivity and compressibility that will be important in determining the pressure at which any hypothetical olivine-melt density crossover may occur.

For liquids that compress in violation of the law of corresponding states, an olivine-liquid density crossover is assured for the range of olivine compositions considered (Figures 5A–C). At 1400°C the hypothetical density crossover is located at a pressure as low as 3 GPa for liquid lherzolite and 5 GPa for MORB (Figure 5A). Again, the density-pressure relations for both MORB and liquid lherzolite are parallel, owing to the similar bulk moduli for each. Furthermore, because the bulk moduli for MORB and liquid lherzolite are much lower than those used in Figs. 4A–C, liquid densities at high pressures are

much higher. For example, the density of liquid lherzolite at 10 GPa is 0.2 gm/cm³ higher when the law of corresponding states is violated.

The conclusion to be drawn from the results in Figures 4 and 5 is that an olivine-liquid density crossover “appears” to exist. However, the pressure at which this apparently occurs is rather uncertain, and ranges from 3 to over 15 GPa, depending on temperature, melt composition, olivine composition, and whether the law of corresponding states is observed.

OLIVINE-MAGMA DENSITY RELATIONS WITH GEOLOGICAL RESTRICTIONS

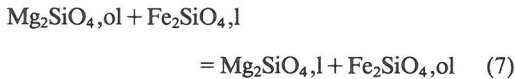
The density of magmas having the compositions of liquid lherzolite, komatiite, and MORB (Table 2) and their coexisting olivine compositions will now be evaluated with a number of geological restrictions imposed. First, the equilibrium compositions of olivine crystals coexisting with the melts have been evaluated, and olivine densities adjusted according to changes in Fe content. Second, densities have not been calculated isothermally. Rather they have been calculated along the anhydrous mantle solidus, the lowermost temperature bound below which anhydrous magmas are not stable. The densities of MORB, komatiite, and liquid lherzolite have been calculated at all pressures along the solidus, although it is recognized that liquid lherzolite is not a stable initial melt composition at 1 atmosphere and MORB is not a stable initial melt composition at high pressures (*e.g.*, OHTANI *et al.*, 1986). Ideally the initial melt compositions at all pressures along the solidus would have to be known, and their densities calculated accordingly. This fine tuning, however, is not required in order to test the olivine flotation hypothesis.

Iron-Magnesium partitioning

For a melt of a known composition the Fe-Mg partition coefficient provides a means for calculating the equilibrium composition of coexisting olivine. The partition coefficient *K_D* takes the form:

$$K_D = \frac{X_{\text{MgO}}}{X_{\text{FeO}}}_{\text{liquid}} \left[\frac{X_{\text{FeO}}}{X_{\text{MgO}}} \right]_{\text{olivine}} \quad (6)$$

is about 0.3 ± 0.03 and relatively insensitive to changes in temperature and composition for basaltic and komatiitic liquids (ROEDER and EMSLIE, 1970; LONGHI *et al.*, 1978; BICKLE, 1982). Pressure increases *K_D* (LONGHI *et al.*, 1978; BICKLE, 1978; HERZBERG *et al.*, 1982) by about 0.1/5 GPa (TAKAHASHI and KUSHIRO, 1983). For the species in the reaction:



the pressure derivative of the distribution coefficient can be evaluated from the relation:

$$\frac{\partial \ln K_D}{\partial P} = \frac{\Delta V}{RT} \quad (8)$$

and the availability of the volume and elastic parameters given in Part 1 (HERZBERG, 1987). The ΔV term was calculated at 2000°C and 1 atmosphere to 20 GPa. The K_D was calculated iteratively with $K_D = 0.3$ at atmospheric pressure as the initial point. The results (Figure 6) are in overall agreement with the experimental observations of TAKAHASHI and KUSHIRO (1983) and BICKLE (1978) although the calculated K_D appears somewhat too high in the 2–3 GPa range. A number of important uncertainties will affect these calculations, including excess volume contributions to ΔV in the melt and olivine phases at high temperatures and pressures, and the composition of the melt (*e.g.*, SiO_2). However, these uncertainties will be masked by the initial range of ± 0.03 in K_D , and the effect propagated to olivine density calculations will be trivial. In the calculations that follow, the compositions of olivine in equilibrium with the coexisting liquids were determined from Figure 6.

Temperature

Both olivine and magma densities were calculated at temperatures along the anhydrous solidus. The solidus for anhydrous garnet lherzolite to 5 GPa, reviewed in HERZBERG (1983), has now been determined experimentally to 20 GPa (TAKAHASHI and SCARFE, 1985; TAKAHASHI, 1986; SCARFE and TAKAHASHI, 1986) for natural Fe-bearing compositions. Experimental data to 13 GPa for compo-

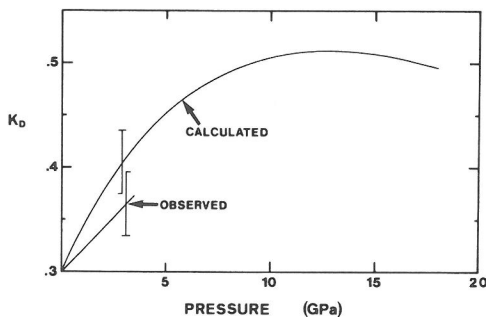


FIG. 6. Calculated and experimentally observed variations in K_D , the partition coefficient of Fe and Mg between olivine and melt, as a function of pressure.

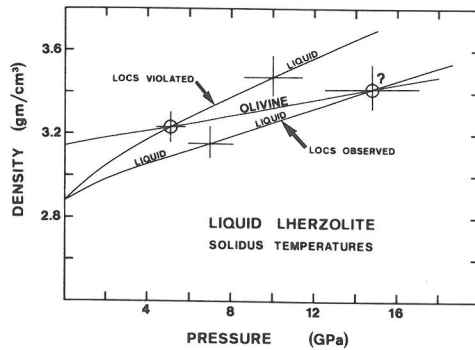


FIG. 7. Densities of liquid lherzolite PHN 1611 calculated with the Law Of Corresponding States (LOCS) observed and violated compared to densities of coexisting olivine. Temperatures are restricted to the anhydrous solidus. Where LOCS is observed the density crossover may be meaningless because olivine may not be a stable liquidus or solidus phase at these pressures.

sitions in the system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ place the solidus at significantly higher temperatures, indicating that FeO reacts with the graphite-diamond heater/container system and produces CO_2 vapor which reduces the anhydrous solidus in natural systems by over 200°C (HERZBERG, in preparation). The temperatures in °C and pressures in GPa of the anhydrous solidus used in these calculations are: 1400, 2; 1620, 4; 1800, 6; 1930, 8; 2020, 10; 2090, 12; 2150, 14; 2190, 16; 2220, 18 (note: the last three are extrapolated).

Numerical results

The densities of liquid lherzolite PHN 1611 and olivines which range from Fo_{95} at 1 atmosphere to Fo_{93} at 18 GPa are shown in Figure 7. Two completely different possibilities emerge, depending upon whether liquids compress according to or in violation of the law of corresponding states. For liquids which compress according to the law of corresponding states, a density crossover is computed at about 15 ± 2 GPa. However, this may be an apparent density crossover rather than a real one because it is within this pressure range where olivine and the liquid lherzolite become unstable. At these pressures, olivine is no longer the liquidus phase for PHN 1611 (HERZBERG, 1983; TAKAHASHI, personal communication). Rather, it is replaced by majorite, a pyroxene-garnet solid solution phase having a garnet crystal structure. Although the high temperature elastic properties for majorite are still poorly constrained, it can be shown that majorite is much denser than liquid lherzolite at these pressures (*e.g.*, see HERZBERG, 1986). Additionally, at

about 16 GPa olivine is replaced by its higher pressure β -phase polymorph, which is denser than olivine by about 0.2 gm/cm^3 . It is concluded that the hypothesis of olivine flotation in lherzolite liquids which compress according to the law of corresponding states is unconvincing. However, owing to the size of the errors in these calculations, the hypothesis can neither be refuted nor supported at the present time. The possibility that olivine flotation may occur at some pressure slightly lower than that required to destabilize olivine cannot be precluded.

For the lherzolite liquid that compresses in violation of the law of corresponding states, the olivine-magma density crossover is located at about $5 \pm 1.5 \text{ GPa}$. Clearly, this elastic model supports unambiguously the olivine flotation hypothesis.

Similar results are obtained for the komatiite composition (Figure 8). Olivine compositions are Fo_{94} at 1 atmosphere to Fo_{90} at 18 GPa. With the law of corresponding states maintained, an apparent density crossover is also located around 15 GPa. However, it has been established by experiment that for analogue compositions in the system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$, olivine becomes replaced by garnet as the liquidus phase in the 6 to 7 GPa range (HERZBERG *et al.*, 1986). Furthermore, the experimental results on lherzolite PHN 1611 indicate that olivines crystallizing from the komatiite will be transformed to the modified spinel polymorph in the 15 GPa range. Indeed, these density comparisons are rendered petrologically meaningless because olivine and komatiite are not in equilibrium at 15 GPa. At pressures where olivine and komatiite are stable (i.e., less than 6 to 7 GPa), olivine is predicted to remain considerably more dense than komatiite. For komatiite compression in violation of the law of corresponding states, the density crossover is located

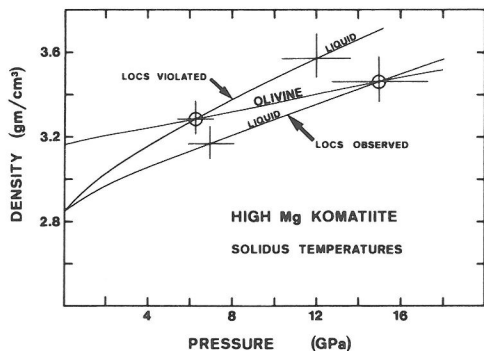


FIG. 8. Densities of high Mg komatiite calculated with the Law Of Corresponding States (LOCS) observed and violated compared to densities of coexisting olivine.

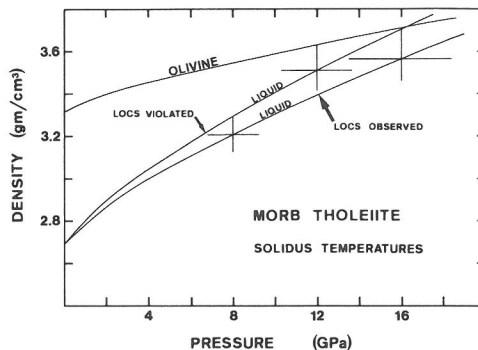


FIG. 9. Densities of MORB tholeiite calculated with the Law Of Corresponding States (LOCS) observed and violated compared to densities of coexisting olivine.

at $6 \pm 1.5 \text{ GPa}$. At pressures less than those required to stabilize liquidus garnet, olivine flotation is a possibility for this elastic model.

The density relations for the MORB composition are shown in Figure 9. Olivine compositions range from Fo_{81} at 1 atmosphere to Fo_{71} at 18 GPa. Because these olivines are so iron-rich compared to those for the komatiite and lherzolite compositions, an apparent density crossover occurs only at extremely high pressures and for the condition where the law of corresponding states is violated. From the inference that olivine is neither a stable liquidus nor subliquidus phase at these pressures, it is predicted that olivine flotation will not be observed.

CONCLUSIONS

The elastic properties of silicate liquids reported in Part 1 (HERZBERG, 1987) have been applied to the calculation of magma densities to high pressures. The algorithm involves the calculation of the bulk modulus of the magma from the bulk moduli of its constituent oxide components mixed in proportion to their volume fractions according to the Voigt-Reuss-Hill approximation. Two elastic models have been entertained. In the first, silicate liquids compress according to the law of corresponding states; the effect of composition on the compressibility of silicate melts is large, and the composition of the melt must be specified. In the second, silicate liquids compress in violation of the law of corresponding states, and all magma compositions compress by similar amounts over any given increment of pressure.

The two contradictory elastic models have been tested. Both are consistent with the shock wave experiments of RIGDEN *et al.* (1984) on molten $\text{An}_{36}\text{Di}_{64}$ (mol percent), but the agreement is much better for the model that obeys the law of corre-

sponding states. The same holds for the density experiments of FUJII and KUSHIRO (1977) and FUJII (1978) on an olivine tholeiite composition to 2.0 GPa. However, olivine flotation and settling experiments on a similar composition to 8.5 GPa is predicted by the model which obeys the law of corresponding states. The model which violates the law of corresponding states is also in major violation of these data.

The densities of a tholeiite, a komatiite, and a liquid lherzolite have been calculated along the anhydrous solidus to about 18 GPa, and have been compared to the densities of their equilibrium olivine compositions. It is demonstrated that the olivine flotation hypothesis is unconvincing for magmas which compress according to the law of corresponding states. Although an olivine-liquid density crossover is invariably computed, it is located at pressures where equilibrium between the two phases is an assumption which is either in doubt or demonstrably invalid. For liquid lherzolite, olivine is replaced by majorite as the liquidus phases at about the same pressure calculated for the apparent density crossover, this being 15 ± 2 GPa. For the komatiite the apparent density crossover is also about 15 GPa, well in excess of the 6 to 7 GPa pressure range required to stabilize garnet on the liquidus. Furthermore, at 15 GPa, olivine is likely to be transformed to its dense modified spinel polymorph for both the komatiite and liquid lherzolite.

The olivine flotation hypothesis is only plausible for silicate liquids which compress in violation of the law of corresponding states. For komatiite and lherzolite liquids, this elastic law predicts the existence of a real olivine-liquid density crossover at 5 to 6 GPa. The predicted pressures of the real and apparent density crossover points are so fundamentally different for each elastic model, that one or the other should be easily falsifiable by experimentation. Presently available constraints from shock wave and Stokes' Law experiments are most consistent with liquids which compress according to the law of corresponding states.

Acknowledgements—The author is indebted to T. Fujii at the Earthquake Research Institute in Tokyo for making available his experimental results prior to publication. Bjorn Mysen and Larry Finger are thanked for their critical reviews and detailed comments.

REFERENCES

- ANDERSON O. L. (1972) Patterns in elastic constants of minerals important to geophysics. In *Nature of the Solid Earth*, (ed. E. D. ROBERTSON), pp. 575–613 McGraw-Hill.
- BICKLE M. J. (1978) Melting experiments on peridotitic komatiites. In *Progress in Experimental Petrology*, Natural Environment Research Council, 4th Report, Series D, No. 11, 187–195.
- BICKLE M. J. (1982) The magnesium contents of komatiitic liquids. In *Komatiites* (eds. N. T. ARNDT and E. G. NISBET), pp. 479–494, Allen and Unwin.
- BIRCH F. (1952) Elasticity and constitution of the earth's interior. *J. Geophys. Res.* **57**, 227–286.
- BOETTCHER A. L., BURNHAM C. W., WINDOM K. E. and BOHLEN, S. R. (1982) Liquids, glasses, and the melting of silicates to high pressures. *J. Geol.* **90**, 127–138.
- BOTTINGA Y. and WEILL D. (1970) Densities of liquid silicate systems calculated from partial molar volumes of oxide components. *Amer. J. Sci.* **269**, 169–182.
- FISHER G. W. and MEDARIS L. G., JR. (1969) Cell dimensions and x-ray determinative curve for synthetic Mg-Fe olivines. *Amer. Mineral.* **54**, 741–753.
- FLEET M. E., HERZBERG C. T., HENDERSON G. S., CROZIER E. D., OSBORNE M. D. and SCARFE C. M. (1984) Coordination of Fe, Ga and Ge in high pressure glasses by Mössbauer, Raman and X-ray absorption spectroscopy, and geological implications. *Geochim. Cosmochim. Acta* **48**, 1455–1465.
- FUJII T. (1978) Viscosity, density and ascending velocity of magma. *Bull. Volcanol. Soc. Japan*, (2nd Series) **23**, 117–130.
- FUJII T. and KUSHIRO I. (1977) Density, viscosity, and compressibility of basaltic liquid at high pressures. *Carnegie Inst. Wash. Yearb.* **76**, 419–424.
- HAZEN R. M. (1977) Effects of temperature and pressure on the crystal structure of ferromagnesian olivine. *Amer. Mineral.* **62**, 286–295.
- HERZBERG C. T., BAKER M. B. and WENDLANDT R. F. (1982) Olivine flotation and settling experiments on the join Mg_2SiO_4 - Fe_2SiO_4 . *Contrib. Mineral. Petrol.* **80**, 319–323.
- HERZBERG C. T. (1983) Solidus and liquidus temperatures and mineralogies for anhydrous garnet-lherzolite to 15 GPa. *Phys. Earth Planet. Inter.* **32**, 193–202.
- HERZBERG C. T. (1986) Internal structures of the Earth and terrestrial planets: constraints from ultrahigh pressure magma density and phase equilibrium relations. In *Silicate Melts*, (ed. C. M. SCARFE), Ch. 10, pp. 279–304, Mineralogical Assoc. of Canada Short Course Handbook, Vol. 12.
- HERZBERG C. T. (1987) Magma density at high pressure Part 1: The effect of composition on the elastic properties of silicate liquids. In *Magmatic Processes: Physicochemical Principles* (ed. B. O. MYSEN). The Geochemical Society Spec. Publ. 1, pp. 25–46.
- HERZBERG C. T., HASABE K. and SAWAMOTO H. (1986) Origin of high Mg komatiites: constraints from melting experiments to 8 GPa. *Trans. Amer. Geophys. Union* **67**, 408.
- KUMAZAWA M. and ANDERSON O. L. (1969) Elastic moduli, pressure derivatives, and temperature derivatives of single-crystal olivine and single-crystal forsterite. *J. Geophys. Res.* **74**, 5961–5972.
- KUSHIRO I. (1982) Density of tholeiite and alkali basalt magmas at high pressures. *Carnegie Inst. Wash. Yearb.* **81**, 305–309.
- LONGI J., WALKER D. and HAYS J. F. (1978) The distribution of Fe and Mg between olivine and lunar basaltic liquids. *Geochim. Cosmochim. Acta* **42**, 1545–1558.
- MELSON W. G., VALIER T. L., WRIGHT T. L., BYERLY G. and NELEN J. (1976) Chemical diversity of abyssal volcanic glass erupted along Pacific, Atlantic, and Indian

- Ocean sea-floor spreading centers. In *The Geophysics of the Pacific Ocean Basin and Its Margin*, pp. 351–367, American Geophysical Union.
- NELSON S. A. and CARMICHAEL I. S. E. (1979) Partial molar volumes of oxide components in silicate liquids. *Contrib. Mineral. Petrol.* **71**, 117–124.
- NESBITT R. W. and SUN S.-S. (1976) Geochemistry of Archaean spinifex-textured peridotites and magnesian an low-magnesian tholeiites. *Earth Planet. Sci. Lett.* **31**, 433–453.
- NIXON P. H. and BOYD, F. R. (1973) Petrogenesis of the granular and sheared ultrabasic nodule suite in kimberlites. In *Lesotho Kimberlites* (ed. P. H. NIXON), pp. 48–56. Lesotho National Development Corporation, Maseru, Lesotho.
- OHTANI E., TAULELLE F. and ANGELL C. A. (1985) Al³⁺ coordination changes in liquid aluminosilicates under pressure. *Nature* **314**, 78–81.
- OHTANI E., KATO T. and HERZBERG C. T. (1986) Stability of lherzolite magmas at solidus temperatures and 20 GPa. *Trans. Amer. Geophys. Union* **67**, 408–409.
- RIGDEN S. M., AHRENS T. J. and STOLPER E. M. (1984) Densities of liquid silicates at high pressures. *Science* **226**, 1071–1074.
- ROEDER P. L. and EMSLIE R. F. (1970) Olivine-liquid equilibrium. *Contrib. Mineral. Petrol.* **29**, 275–289.
- SCARFE C. M. and TAKAHASHI I. (1986) Melting of garnet peridotite to 13 GPa and the early history of the upper mantle. *Nature* **322**, 354–356.
- STOLPER E., WALKER D., HAGAR B. and HAYS J. (1981) Melt segregation from partially molten source regions: the importance of melt density and source region size. *J. Geophys. Res.* **86**, 6261–6271.
- SUMINO Y. (1979) The elastic constants of Mn₂SiO₄, Fe₂SiO₄ and Co₂SiO₄, and the elastic properties of olivine group minerals at high temperature. *J. Phys. Earth* **27**, 209–238.
- SUZUKI I., ANDERSON O. L. and SUMINO Y. (1983) Elastic properties of a single-crystal forsterite Mg₂SiO₄, up to 1200°K. *Phys. Chem. Minerals* **10**, 38–46.
- SUZUKI I., SEYA K., TAKEI H. and SUMINO Y. (1981) Thermal expansion of fayalite, Fe₂SiO₄. *Phys. Chem. Minerals* **7**, 60–63.
- TAKAHASHI E. (1986) Melting of a dry peridotite KLB-1 up to 14 GPa: implications on the origin of peridotitic upper mantle. *J. Geophys. Res.* **91**, 9367–9382.
- TAKAHASHI E. and KUSHIRO I. (1983) Melting of a dry peridotite at high pressures and basalt magma genesis. *Amer. Mineral.* **68**, 6261–6271.
- TAKAHASHI E. and SCARFE C. M. (1985) Melting of peridotite to 14 GPa and the genesis of komatiite. *Nature* **315**, 566–568.

APPENDIX I

```

1 PRINT "THIS MAGMA DENSITY PROGRAM IS BASED ON AN ELASTIC MODEL WHEREIN"
2 PRINT "SILICATE LIQUIDS COMPRESS ACCORDING TO THE LAW OF CORRESPONDING"
3 PRINT "STATES. PARAMETERS FOR A VIOLATED LAW ARE RETRIEVABLE IN PART 1"
10 DIM N$(7),M9(7),WT(7),D1(7),D2(7),D3(7),CM1(7),CM2(7),CM3(7),ALFA(7),K1(7),K2(7),
    K3(7),KR(3),KV(3),VR(3),G(7)
20 FOR I=1 TO 7:READ N$(I):NEXT I
30 DATA SI02,AL2O3,FeO,MgO,CAO,NA2O,K2O
40 FOR I=1 TO 7:READ M9(I):NEXT I
50 DATA 60.085,101.962,71.846,40.311,56.079,61.979,94.203
60 PRINT:INPUT"SAMPLE NAME:"$:PRINT
70 FOR I=1 TO 7
80 PRINT"WEIGHT % ";N$(I);"="";INPUT WT(I)
90 WT(I)=WT(I)/M9(I)
100 SUMML=SUMML+WT(I)
110 NEXT I
120 FOR I=1 TO 7:WT(I)=WT(I)/SUMML:NEXT I
130 INPUT"TEMPERATURE IN CENTIGRADE";T
140 INPUT"PRESSURE IN KILOBARS";P
160 RESTORE 180
170 FOR I=1 TO 7:READ ALFA(I):NEXT I
180 DATA .000011,.000062,.000236,.000234,.000243,.000247,.000261
190 DELTAT=T-1400
200 FOR I=1 TO 7:READ D1(I),D2(I),D3(I):NEXT I
210 DATA 27.08,26.89,27.27,36.83,36.36,37.30,13.31,12.93,13.69,11.87,11.5,12.24
220 DATA 16.49,16.21,16.77,28.82,28.60,29.04,46.05,45.66,46.44
230 SUM1=0:SUM2=0:SUM3=0
240 FOR I=1 TO 7
250 CM1(I)=WT(I)*D1(I)*(1+ALFA(I)*DELTAT)
260 CM2(I)=WT(I)*D2(I)*(1+ALFA(I)*DELTAT)
270 CM3(I)=WT(I)*D3(I)*(1+ALFA(I)*DELTAT)
280 SUM1=SUM1+CM1(I):SUM2=SUM2+CM2(I):SUM3=SUM3+CM3(I)
290 NEXT I
300 FOR I=1 TO 7
310 V1(I)=CM1(I)/SUM1
320 V2(I)=CM2(I)/SUM2
330 V3(I)=CM3(I)/SUM3
340 NEXT I
350 FOR I=1 TO 7:READ K1(I),K2(I),K3(I):NEXT I

```

```

360 DATA 130,117,143,209,164,254,736,616,859,848,709,991,566,474,657,141,80,199,80,39,113
370 FOR I=1 TO 3:KR(I)=0:KV(I)=0:VR(I)=0:NEXT I
380 FOR I=1 TO 7
390 KR(1)=KR(1)+V1(I)/K1(I)
400 KR(2)=KR(2)+V2(I)/K2(I)
410 KR(3)=KR(3)+V3(I)/K3(I)
420 KV(1)=KV(1)+V1(I)*K1(I)
430 KV(2)=KV(2)+V2(I)*K2(I)
440 KV(3)=KV(3)+V3(I)*K3(I)
450 NEXT I
460 FOR I=1 TO 3
470 KR(I)=1/KR(I)
480 VR(I)=(KR(I)+KV(I))/2
490 NEXT I
500 SG=0
510 FOR I=1 TO 7
520 G(I)=WT(I)*M9(I)
530 SG=SG+G(I)
540 NEXT I
550 D1=SG/SUM1:D2=SG/SUM2:D3=SG/SUM3
560 DP1=D1:DD=.5
570 DP1=DP1+DD
580 Z1=Z
590 Z=1.5*VR(1)*((DP1/D1)2.333-(DP1/D1)1.667)
600 IF Z<P AND Z>Z1 THEN 570
610 IF Z<P AND Z<Z1 THEN DD=DD/2:GOTO 570
620 IF Z>P AND Z>Z1 THEN DD=DD/2:DP1=DP1-DD:GOTO 580
630 IF Z>P AND Z<Z1 THEN DP1=DP1-DD:GOTO 580
640 P2 = 3/2*VR(2)*((DP1/D1)2.333 - (DP1/D1)1.667)
650 P3 = 3/2*VR(3)*((DP1/D1)2.333 - (DP1/D1)1.667)
660 DP2 = DP1 - D1 + D3
670 DP3 = DP1 + D2 - D1
680 DP4 = D1:DD=.5
690 DP4 = DP4 + DD
695 Z1 = Z
700 Z = 1.5*VR(2)*((DP4/D1)2.333-(DP4/D1)1.667)
710 IF Z<P AND Z>Z1 THEN 690
720 IF Z<P AND Z<Z1 THEN DD=DD/2:GOTO 690
730 IF Z>P AND Z>Z1 THEN DD=DD/2:DP4=DP4-DD:GOTO 695
740 IF Z>P AND Z<Z1 THEN DP4=DP4-DD:GOTO 695
750 DP5 = D1:DD=.5
760 DP5 = DP5+DD
770 Z1 = Z
780 Z=1.5*VR(3)*((DP5/D1)2.333-(DP5/D1)1.667)
790 IF Z<P AND Z>Z1 THEN 760
800 IF Z<P AND Z<Z1 THEN DD=DD/2:GOTO 760
810 IF Z>P AND Z>Z1 THEN DD=DD/2:DP5=DP5-DD:GOTO 770
820 IF Z>P AND Z<Z1 THEN DP5=DP5-DD:GOTO 770
830 DUP1 = DP3 - DP1
840 DUP2 = DP4 - DP1
850 DDWN1 = DP1 - DP2
860 DDWN2 = DP1 - DP5
870 DUP = (DUP12 + DUP22).5
880 DDWN = (DDWN12 + DDWN22).5
890 CLS
900 LPRINT"SAMPLE NAME: ";NA$
910 LPRINT "TEMPERATURE ="; T;"C"
920 LPRINT USING "DENSITY AT 1 ATMOSPHERE = ### GM/CC RANGE = ### TO ###",D3,D2
930 LPRINT "FOR PRESSURE ="; P;"KILOBARS"
940 LPRINT USING "DENSITY = ### GM/CC RANGE = ### TO ###"; DP1,DP1-DDWN,DP1+DUP
950 LPRINT USING "PRESSURE RANGE = ### TO ### KBAR",P,P3
960 LPRINT USING "BULK MODULUS = ### KILOBARS RANGE = ### TO ###"(1),VR(2),VR(3)
970 LPRINT
980 PRINT "DO YOU WANT A CHANGE OF TEMPERATURE OR PRESSURE? (Y/N)"
990 Y$=INPUT$(1):IF Y$="" THEN 990
1000 IF Y$="Y" OR Y$="y" THEN 130
1010 END

```

APPENDIX II

```
10 INPUT "MOLE FRACTION FORSTERITE";XMG
20 INPUT "TEMPERATURE IN CENTIGRADE";T
30 INPUT "PRESSURE IN KILOBARS";P
40 MASS = 203.777 - 63.07*XMG
50 V = (307.23 - 15.49*XMG - 2.02*XMG2)*.15055
60 ALFA = (9.7E-09 + XMG*6E-10)*T + .0000255 + XMG*.0000019
70 V0 = V*(1 + ALFA*(T-25))
80 KOL = (-.2775 + XMG*.0504)*T + 1380 - 96.7*XMG
90 KDL = 5.39
100 D1 = MASS/V0
110 DP1 = D1:DD = .5
120 DP1 = DP1 + DD
130 Z1 = Z
140 Z = 1.5*KOL*((DP1/D1)2.333 - (DP1/D1)1.667)*(1-.75*(4-KDL)*((DP1/D1)1.667 - 1))
150 IF Z < P AND Z > Z1 THEN 120
160 IF Z < P AND Z < Z1 THEN DD = DD/2:GOTO 120
170 IF Z > P AND Z > Z1 THEN DD = DD/2:DP1 = DP1 - DD:GOTO 130
180 IF Z > P AND Z < Z1 THEN DP1 = DP1 - DD:GOTO 130
190 LPRINT "MOLE FRACTION FORSTERITE IN OLIVINE =" XMG
200 LPRINT "TEMPERATURE =" T;"C"
210 LPRINT "PRESSURE =" P;"KILOBARS"
220 LPRINT USING "OLIVINE DENSITY AT 1 ATM = ### GM/CC";MASS/V0
230 LPRINT USING "OLIVINE DENSITY AT P = ### GM/CC";DP1
240 LPRINT
250 END
```