

Melting of Enstatite (MgSiO_3) From 10 to 16.5 GPa and the Forsterite (Mg_2SiO_4) - Majorite (MgSiO_3) Eutectic at 16.5 GPa: Implications for the Origin of the Mantle

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A split sphere multianvil apparatus (USSA 2000) has been used to determine the melting curve of enstatite (MgSiO_3) from 10 to 16.5 GPa and the forsterite (Mg_2SiO_4) - majorite (MgSiO_3) eutectic at 16.5 GPa. Use of a new capsule material, rhenium, allowed long runs of up to 2 hours at temperatures up to 2380°C with no observed contamination of the sample and with stable temperature control. Melting temperatures of enstatite are up to 160°C higher than those of Kato and Kumazawa (1986a). Two invariant points have been located, one for orthoenstatite + clinoenstatite + liquid at 2230°C, 11.9 GPa, and one for clinoenstatite + majorite + liquid at 2370°C, 16.4 GPa. Forsterite melts incongruently at 2350°C, 16.5 GPa to liquid and Anhb ($\text{Mg}_{14}\text{Si}_5\text{O}_{24}$). In the system Mg_2SiO_4 - MgSiO_3 at 16.5 GPa, the forsterite-majorite eutectic has been located at 34 wt % Mg_2SiO_4 , a composition similar to that determined by Kato and Kumazawa (1986a) at 20 GPa but much lower in Mg_2SiO_4 than several previous estimates based on melting experiments on mantle peridotite compositions. This forsterite-poor location for the eutectic is in apparent conflict with the suggestion that the peridotitic upper mantle is a crystallized eutectic-like liquid formed at about 16 GPa.

INTRODUCTION

Differentiation of the Earth into crust, mantle, and core is generally considered to have involved early melting of major portions or perhaps all of the Earth [e.g., Kaula, 1979; Anderson, 1982; Nisbet and Walker, 1982; Herzberg and O'Hara, 1985; Ohtani, 1985; Scarfe and Takahashi, 1986]. A rigorous discussion of this subject requires an understanding of liquidus phase relationships at all depths in the Earth. Due to recent improvements in the design of multianvil presses [Kumazawa and Endo, 1984], melting studies of mantle materials can now be carried out routinely at pressures in excess of 20 GPa. Two of the most important minerals relevant to the Earth's mantle are forsterite and enstatite along with their high-pressure transformation products. In this paper we present the melting curve of enstatite from 10 to 16.5 GPa and liquidus phase relationships for the system Mg_2SiO_4 - MgSiO_3 at 16.5 GPa.

PREVIOUS LIQUIDUS STUDIES

Bowen and Andersen [1914] studied the system MgO - SiO_2 at atmospheric pressure and showed that enstatite melts incongruently to liquid and forsterite. Liquidus phase relationships at high pressures remained unknown until half a century later when the piston-cylinder apparatus was developed [Boyd and England, 1960]. Several studies followed. Davis and England [1964] determined the melting curve of forsterite up to 5 GPa. Boyd *et al.* [1964], in their study of the melting behavior of enstatite up to 4.7 GPa, found that it melts congruently at high pressures beginning at some pressure less than 0.54 GPa. Chen and Presnall [1975] documented the shift of the eutectic between forsterite and enstatite with increasing pressure and

estimated the pressure of the singular point at which enstatite begins to melt congruently to be about 0.13 GPa.

More recent studies with the multianvil apparatus have extended knowledge of liquidus phase relationships to pressures beyond the range of the piston-cylinder apparatus. Ohtani and Kumazawa [1981] showed a simple congruent melting curve for forsterite up to 15 GPa but stated that they were confident of its congruent melting behavior only at pressures less than 12.7 GPa. Kato and Kumazawa [1985a] found a field of periclase + liquid at 15 and 20 GPa for an Mg_2SiO_4 starting composition, which would imply incongruent melting at these pressures. They subsequently described an additional complexity in the melting of Mg_2SiO_4 at 20 GPa [Kato and Kumazawa, 1986a]; beta phase (modified spinel) was found to melt incongruently to phase B + liquid at 2250°C, with phase B then melting incongruently to periclase + liquid at 2300°C. Kato and Kumazawa [1985b, 1986a] determined melting temperatures of enstatite at 3 and 7 GPa that are consistent with the melting curve determined by Boyd *et al.* [1964] and with extrapolation of this curve using the Simon equation. However, at 20 GPa, Kato and Kumazawa's melting temperature of 2250°C implies a significant reduction in the dT/dP slope of the enstatite melting curve beginning at about 7 GPa, a feature that would not have been predicted on the basis of an extrapolation of the data at lower pressures. Kato and Kumazawa [1985b, 1986a] also studied melting relationships in the system Mg_2SiO_4 - MgSiO_3 at 3, 7, and 20 GPa and found that the shift of the forsterite-enstatite eutectic toward forsterite with pressure becomes progressively less pronounced as pressure increases.

EXPERIMENTAL PROCEDURE

The experiments were performed with the split sphere multianvil apparatus [USSA-2000] at the State University of New York at Stony Brook. A description of this apparatus is given by Remsberg *et al.* [1988] and Gasparik [1989]. An MgO octahedron with a 10-mm edge length and WC cubes with 5-mm truncations were used for all experiments. Gaskets were

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of pyrophyllite and were backed up by teflon strips. Figure 1 shows a cross section through the octahedron. Temperatures were measured and controlled with a W3Re/W25Re thermocouple positioned axially within a cylindrical LaCrO₃ heater and resting with its tip in contact with the sample capsule. Temperatures were not corrected for the effect of pressure on the thermocouple emf. The pressure calibration is the same as that carried out at high temperatures by Gasparik [1989]. This calibration is based on the coesite-stishovite transition at 1200°C, 9.3 GPa and 1400°C, 9.5 GPa [Yagi and Akimoto, 1976], and the clinoenstatite to beta phase + stishovite transition at 1400°C, 16.5 GPa [Gasparik, 1989]. The curvature of the calibration curve is drawn to conform to the curvature of the room temperature calibration defined by several fixed points [see Gasparik, 1989].

To remove any traces of water, the complete octahedron assembly, including the sample capsule, was fired for 1 hour at 1000°C in argon immediately prior to an experiment. Canil and Scarfe [this issue] have shown that even when this drying procedure is followed, a small amount of water forms in the capsule, apparently by diffusion of H₂ from dehydration of the pyrophyllite gaskets. However, because their assembly (graphite heater, Pt capsule, and a thermocouple that passes through a hole in the zirconia sleeve and graphite heater at the hot spot) has some differences from ours (Figure 1), their findings may not apply to our assembly. In any case, no hydrous phases were found in the quenched runs, and 58 microprobe spot analyses of liquid regions (crystalline after quenching) of the charges gave totals between 99.04 and 100.82 wt %, with an average of 99.65 wt %. Therefore, we believe our experiments were either anhydrous or nearly so.

A new feature of the pressure cell assembly is the use of rhenium capsules. This metal was tried because of its malleability and extremely high melting temperature at atmospheric pressure (3180°C). As a preliminary test, a fragment of Re was placed inside a Pt capsule together with a forsterite-enstatite mixture and run at 1750°C, 2.0 GPa for 1 hour in a piston-cylinder apparatus. Microprobe examination showed no Re in the glass immediately surrounding the Re fragment and no evidence of any other reaction between the Re and the glass.

Experiments with Re capsules in the multianvil apparatus were very successful. Use of these capsules resulted in an

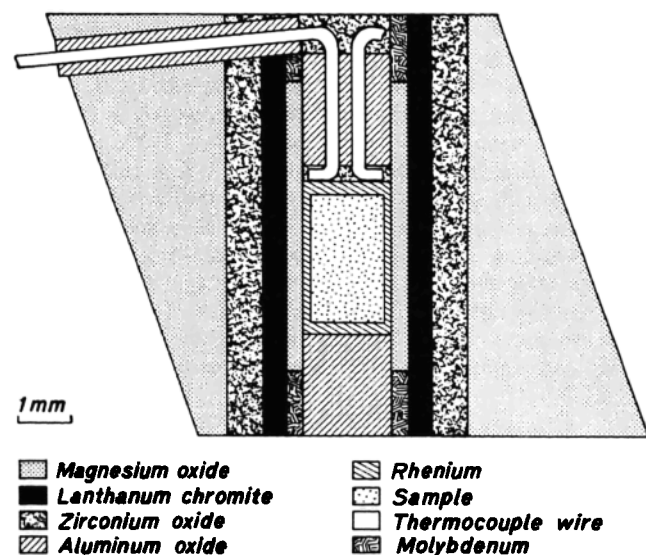


Fig. 1. Assembly of 10-mm octahedron.

ability to carry out long melting experiments at very high temperatures with no observed contamination of the sample from the pressure cell assembly. The most severe conditions attempted were 2430°C, 16.5 GPa for 2 hours, and under these conditions, no melting of the various ceramic parts of the pressure cell assembly was observed. Because power consumption during these long experiments remained very stable, we believe that the thermocouples did not drift significantly.

Five starting materials were used. Three were prepared as oxide mixtures with the compositions MgSiO₃; 80% MgSiO₃, 20% Mg₂SiO₄; and 40% MgSiO₃, 60% Mg₂SiO₄ by weight. Each mixture was fired at 1650°C for 2 hours, quenched, crushed, and fired a second time under the same conditions. The second crushed glass was then recrystallized at 1450°-1500°C for 3 hours. The other two starting materials with the starting compositions MgSiO₃ and Mg₂SiO₄ were prepared by sintering oxide mixtures at 1300°C for 24 hours, grinding, and sintering again under the same conditions. All starting mixtures yielded internally consistent data.

As described by Gasparik [1989] and Herzberg *et al.* [this issue], the sample capsule was positioned with the hot spot within the capsule but near the end in contact with the thermocouple. In this configuration, the thermocouple lies just off the hot spot (Figure 2). For a multicomponent system, in which the liquid composition would be a strong function of temperature, the large temperature variations shown in Figure 2 would be undesirable. However, for a one-component system, this variation is an advantage because more than one phase transition can sometimes be located in the same experiment. For an experiment that straddles the temperature of a phase transition, the boundary between the two phase assemblages is typically a sharp and easily distinguished curved line that follows an isotherm in the capsule. Comparison of the position of this boundary in a polished longitudinal section with Figure 2 yields the phase boundary temperature within about 30°C.

For liquidus experiments, glasses were never produced, but the feathery texture of the quench crystals allowed them to be distinguished easily from equilibrium crystals. Polymorphs of

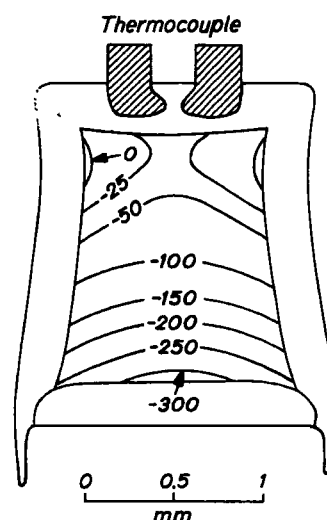


Fig. 2. Relative temperature contours (°C) for experiments in the temperature range 2000°-2150°C. Contours are interpolations based on Figure 3 of Herzberg *et al.* [this issue] with slight modifications of shape based on crystal-liquid isothermal surfaces observed in this study. The pressure cell assembly of Herzberg *et al.* [this issue] is identical to that used here except for their use of Mo capsules. The temperature difference of 300°C between the hot and cold ends of the capsule is consistent with the smaller difference of 200°C reported by Gasparik [1989] at lower temperatures (1400°-1700°C).

enstatite were distinguished optically in transmitted light; orthoenstatite has parallel extinction and low birefringence, clinoenstatite has inclined extinction and high birefringence, and majorite is nearly isotropic. Fluorescence colors under the electron microprobe beam (clinopyroxene, fairly bright and pale blue; majorite, barely visible; forsterite, dim purple; beta phase, bright green) also were very useful.

Electron microprobe analyses were performed on the Cameca MBX instrument at State University of New York at Stony Brook using synthesized crystalline MgSiO_3 as a standard. For some of the samples, additional microprobe examination was carried out on the JEOL 8600 instrument at University of Texas at Dallas.

MELTING CURVE OF ENSTATITE

Figure 3 shows the phase diagram for MgSiO_3 up to 16.5 GPa. Points on the curves refer to temperatures of phase boundary interfaces within the capsules, not to nominal run temperatures. Because smooth curves can be drawn within 20°C of all the data points, we believe the assigned $\pm 30^\circ\text{C}$ uncertainty is conservative. Table 1 gives the experimental run conditions. Two invariant points have been located, one for orthoenstatite + clinoenstatite + liquid at 2230°C , 11.9 GPa, and one for clinoenstatite + majorite + liquid at 2370°C , 16.4 GPa. The determined position of the orthoenstatite-clinoenstatite-liquid invariant point lies along a straight-line extension of the reversed orthoenstatite-clinoenstatite transition boundary determined by *Pacalo and Gasparik* [1989] from 900° to 1700°C . Because the pressure calibration at high temperatures (1200° – 1400°C) used by *Pacalo and Gasparik* [1989] is the same as that used here, the consistency between the two data sets indicates that the pressure calibration remains valid at temperatures at least up to about 2250°C .

Figure 4 shows that our melting temperatures are up to 160°C higher than those of *Kato and Kumazawa* [1985b, 1986a] and that the difference increases with pressure. This difference is probably due to contamination of their samples by Al_2O_3 , CaO , and possibly H_2O , which they documented [*Kato and Kumazawa*, 1986a]. If complications involving the protoenstatite-orthoenstatite boundary are ignored, the melting curve

consists of three segments separated by slope discontinuities at the two invariant points, orthoenstatite-clinoenstatite-liquid and clinoenstatite-majorite-liquid. No discontinuity in the slope occurs at the singular point at which enstatite changes from incongruent to congruent melting behavior (about 0.13 GPa [*Chen and Presnall*, 1975]). A precise algebraic description of the melting curve would require a separate equation to be fitted to each of the three segments, but our data are not sufficiently precise to resolve the changes in slope (required by Schreinemakers' rules) at the two invariant points. Therefore, we have fitted a single Simon equation

$$P = 2.61[(T/1832)^{5.39} - 1]$$

to the entire melting curve up to 16.5 GPa. The constant, 1832, is the incongruent melting temperature of protoenstatite at atmospheric pressure [*Chen and Presnall*, 1975], T is in degrees K, and P is in GPa. This equation fits our data and the lower pressure data of *Boyd et al.* [1964] but gives temperatures slightly lower than those indicated by the data of *Chen and Presnall* [1975, Figures 4 and 5] at pressures from 0.6 to 1.2 GPa. The slightly higher temperatures indicated by *Chen and Presnall* may be related to complications in the melting curve in this pressure range associated with the protoenstatite-orthoenstatite inversion.

CLINOENSTATITE-MAJORITE TRANSITION

The negative slope of the clinoenstatite-majorite transition (Figure 3) is indicated by two independent observations. First, the clinoenstatite to beta phase + stishovite transition has a slightly positive slope and meets the clinoenstatite-stishovite-majorite-beta phase invariant point at 1600°C , 16.7 GPa (Figure 3 and *Gasparik* [1989]). This location is close to that given by *Sawamoto* [1987] at 1650°C , 17 GPa. Our run at a nominal temperature of 2350°C , 16.5 GPa shows majorite at the liquidus, which forces the majorite-clinoenstatite-liquid invariant point below 16.5 GPa. Therefore, the slope of the clinoenstatite-majorite transition curve must be negative. Second, the run on the En1 starting composition at a nominal temperature of 2200°C , 16.5 GPa (Table 1) shows clinoenstatite in the cold end of the capsule and majorite in the hot end, and the

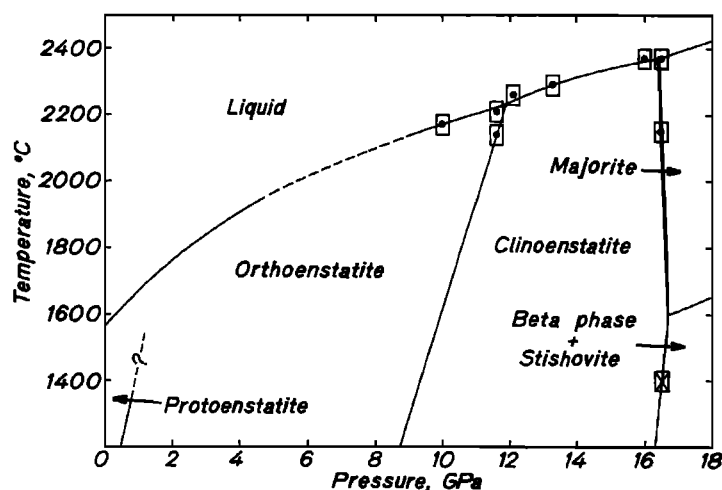


Fig. 3. Phase diagram for MgSiO_3 . Points with dots indicate temperatures of phase boundaries within capsules, not nominal run temperatures. The point with a cross is from *Gasparik* [1989]. Rectangles indicate uncertainty. The orthoenstatite-clinoenstatite transition at temperatures below 1700°C is from *Pacalo and Gasparik* [1989]; the clinoenstatite + majorite + stishovite + beta phase invariant point is from *Gasparik* [1989]; the melting curve up to 4.7 GPa is from *Boyd et al.* [1964] and *Chen and Presnall* [1975]; and the protoenstatite-orthoenstatite transition is from *Anastasiou and Seifert* [1972], *Kushiro et al.* [1968], and *Chen and Presnall* [1975].

TABLE 1. Experiments With the Multianvil Apparatus

| Starting Composition ^a | P, GPa | T, °C | | Time, min |
|-----------------------------------|--------|---------|-----------------------|-----------|
| | | Nominal | Boundary ^b | |
| En1 | 10.0 | 2150 | 2170(L) | 21 |
| En1 | 11.6 | 2200 | 2210(L) | 13 |
| | | | 2140(OC) | |
| En2 | 12.1 | 2230 | 2260(L) | 4 |
| En2 | 13.3 | 2250 | 2290(L) | 11 |
| En1 | 16.0 | 2340 | 2370(L) | 60 |
| En2 | 16.5 | 2350 | 2370(L) | 30 |
| | | | 2150(CM) | |
| Fo | 16.5 | 2380 | 2350(P) | 120 |
| 80En | 16.5 | 2200 | 2250(E) | 60 |
| | | | 2150(CM) | |
| 40En | 16.5 | 2200 | 2240(E) | 60 |
| | | | 2230(FB) | |
| | | | 2130(CM) | |

^aEn1, recrystallized glass (clinoenstatite); En2, 75% clinoenstatite, 25% orthoenstatite, sintered oxide mixture; Fo, Mg₂SiO₄, sintered oxide mixture; 80En, 20 wt % Mg₂SiO₄, 80 wt % MgSiO₃, recrystallized glass; 40En, 60 wt % Mg₂SiO₄, 40 wt % MgSiO₃, recrystallized glass.

^bAbbreviations for phase boundaries: L, liquidus; E, (forsterite + majorite)/liquid eutectic; P, forsterite/(AnhB + liquid) peritectic; OC, orthoenstatite/clinoenstatite; CM, clinoenstatite/majorite; FB, forsterite/beta phase.

boundary between clinoenstatite and majorite follows the expected contour of an isotherm within the capsule. This is the opposite result of an experiment by Kato and Kumazawa [1986a, p. 9353] at 20 GPa, 2250°C. If the difference in pressure, which might be due to the different pressure calibration procedures used, is ignored, the result of Kato and Kumazawa seems explainable only if a pressure gradient existed in their capsule, with the cool part of the capsule being at higher pressure. A gradient of this type has been shown to exist by Gasparik [1989] at room temperature and may also exist at high temperatures. Because the curve is nearly independent of temperature, only a small pressure gradient would cause the positions of majorite and clinoenstatite in the capsule to be interchanged. Our longer run time (1 hour versus 2 min for the experiment of Kato and Kumazawa) would be expected to result in greater relaxation of stress differences. The equation for the majorite-clinoenstatite transition is

$$P = 17.36 - 0.0004T$$

with P expressed in GPa and T in °C.

One might argue that clinoenstatite in the cold end of the capsule is simply unreacted and metastable pyroxene from the

starting material or produced during initial pressurization of the sample. If so, the presence of this unreacted pyroxene should not be sensitive to small variations in the pressure of the run at constant temperature. At the University of Alberta, Canada, one of us (D. C. Presnall) carried out a series of three 1-hour experiments all at 2050°C and at 0.2 GPa intervals using the same pressure cell assembly and recrystallized glass starting material used here. At the lowest of the three pressures, clinoenstatite was found throughout the capsule; at the highest pressure, majorite was found throughout; and at the intermediate pressure, clinoenstatite was found in the cold end and majorite in the hot end of the capsule. These results show that temperatures even in the cold end of the capsule are sufficient for the formation of majorite in 1-hour runs.

THE SYSTEM Mg₂SiO₄-MgSiO₃ AT 16.5 GPa

Figure 5 shows liquidus phase relationships for the system Mg₂SiO₄-MgSiO₃ at 16.5 GPa. It is based on four experiments. One on the En2 starting composition shows the melting temperature of majorite at 2370°C (Table 1). A second experiment on the Fo starting composition at a nominal temperature of 2380°C (Table 1) shows the incongruent melting of beta phase to liquid plus a phase with the stoichiometry, Mg₁₄Si₅O₂₄ (see analysis in Table 2), to which Finger *et al.* [1989] have given the name AnhB (for anhydrous phase B), and which Herzberg and Gasparik [1989] first discovered. The sample of AnhB studied by Finger *et al.* was taken from the run on Mg₂SiO₄ composition listed in Table 1. AnhB is isostructural with Mg₁₄Ge₅O₂₄ [Von Dreele *et al.*, 1970; Finger *et al.*, 1989] and has an Mg/Si ratio only slightly lower than that of phase B, Mg₁₂Si₄O₁₉(OH)₂ [Finger *et al.*, 1989]. Kato and Kumazawa [1986b] and Ito and Takahashi [1987] reported microprobe analyses of what they thought was the hydrous phase B, but found oxide sums close to 100%. We suggest, with Herzberg and Gasparik [1989], that the phase found by Kato and Kumazawa [1986a; 1986b] and Ito and Takahashi [1987] is probably AnhB.

Periclase was also found in the run at 2380°C (Table 2) as inclusions within AnhB grains. On the basis of the finding by Presnall and Walter [1989] that forsterite melts incongruently to periclase + liquid from 10.5 to 16 GPa, we interpret this result to indicate that at 16.5 GPa forsterite melts incongruently to AnhB + liquid and that AnhB then melts incongruently to periclase + liquid at a higher temperature. This interpretation is based on the fact that an invariant point in P-T space must exist at about 16 GPa where the incongruent melting reaction changes from forsterite = periclase + liquid to forsterite = AnhB + liquid [Presnall and Walter, 1989]. At pressures

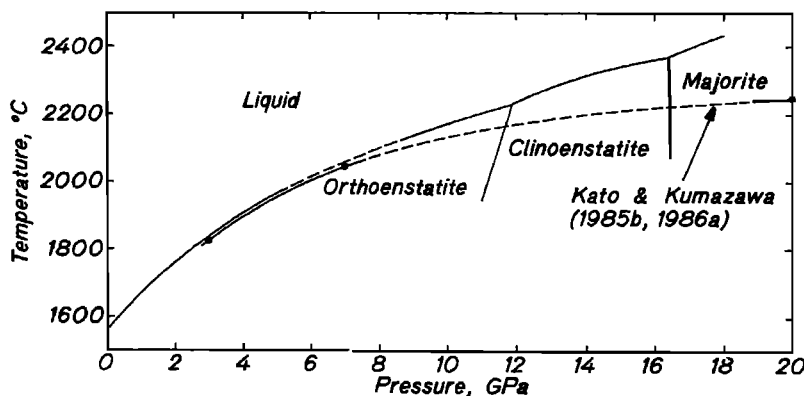


Fig. 4. Comparison of melting curve of this study with that of Kato and Kumazawa [1985b, 1986a].

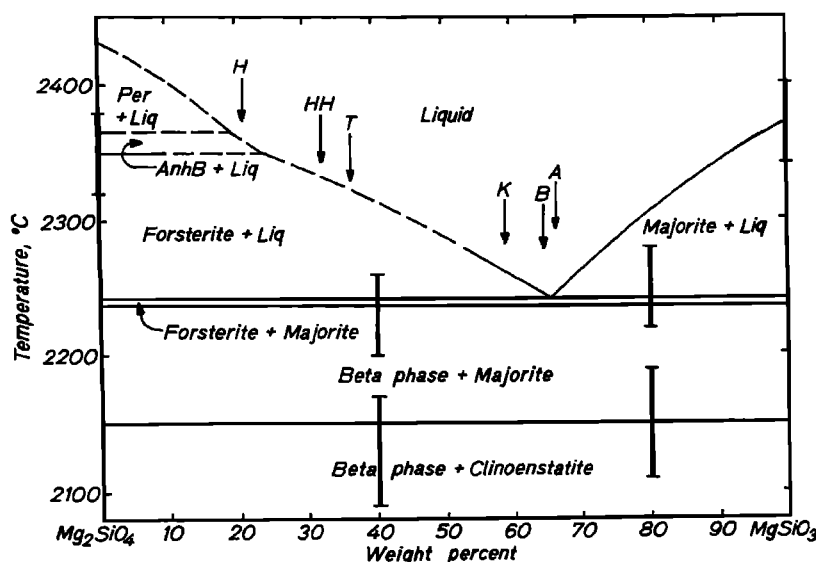


Fig. 5. The system Mg_2SiO_4 - MgSiO_3 at 16.5 GPa. Brackets indicate uncertainty. The bracket at 2350°C refers to the reaction, Forsterite = Anhb + Liquid; those at 2240°C and 2250°C refer to the eutectic temperature. Labels are as follows: A, average of 26 spot analyses of the quenched liquid from the experiment on 80En at 16.5 GPa (Tables 1 and 3); B, average of 31 spot analyses of the quenched liquid from the experiment on 40En at 16.5 GPa (Tables 1 and 4); K, composition of beta phase-majorite eutectic determined by Kato and Kumazawa [1986a] at 20 GPa; H, HH, and T, compositions of forsterite-majorite eutectic inferred by Herzberg and O'Hara [1985] at 15 GPa, by Herzberg *et al.* [1988] and Herzberg and Ohtani [1988] at 16 GPa, and by Takahashi [1986] at 16 GPa, respectively.

above that of the invariant point at 16 GPa, Schreinemaker's rules require the existence of the univariant curve, $\text{Anhb} = \text{periclasite} + \text{liquid}$, and they require further that this curve must lie at higher temperatures than the univariant curve, $\text{forsterite} = \text{Anhb} + \text{liquid}$. The results of Kato and Kumazawa [1986a] at 20 GPa support this same sequence of reactions with increasing temperature if phase B reported by them is actually Anhb.

A third experiment on the starting composition 80En at a nominal temperature of 2200°C (Table 1) shows the majorite + beta phase to clinoenstatite + beta phase transition in the cooler half of the capsule at a temperature of 2150°C. At the hottest part of the capsule, a thin layer of majorite is sandwiched between quench crystals and the subsolidus assemblage, majorite + forsterite, at a temperature of 2250°C. (The sample was damaged before identification of the form of Mg_2SiO_4 at the solidus could be made, but on the basis of the results on 40En at the same pressure and temperature, it is assumed to be forsterite.) Thus, the eutectic must lie toward forsterite from the bulk composition of the mixture. Microprobe spot analyses

TABLE 2. Compositions of Phases From the Experiment on Mg_2SiO_4 at 2380°C (Nominal) and 16.5 GPa

| Oxides, wt % | | | Cations | | |
|--------------------------------|------------------|-------|---------|-------|--------|
| MgO | SiO ₂ | Total | Mg | Si | Total |
| <i>Beta Phase^a</i> | | | | | |
| 56.88 | 41.89 | 98.77 | 2.012 | 0.994 | 3.006 |
| <i>Anhb^b</i> | | | | | |
| 64.44 | 34.13 | 98.57 | 14.028 | 4.984 | 19.012 |
| <i>Periclasite^c</i> | | | | | |
| 99.24 | | 99.24 | | | |

^aCold end of sample, average of three analyses, cations/4 oxygens.

^bMiddle of sample, average of nine analyses, cations/24 oxygens.

^cInclusions in Anhb, average of four analyses.

in the area of quench crystals yielded compositions ranging from 51.0 to 74.7 wt % MgSiO_3 (Table 3). This variation is interpreted to be the result of varying proportions of quench forsterite and majorite intersected by the electron beam, which was not broadened. The average composition of 26 microprobe spot analyses (Table 3) is 66.6 wt %.

A fourth experiment on 40En (Table 1) shows the eutectic at 2240°C, with a band of forsterite (sometimes beta phase) separating the subsolidus forsterite + majorite (sometimes beta phase + majorite) assemblage from the quenched liquid region.

TABLE 3. Compositions of Phases From the Experiment on 80En at 2200°C (Nominal) and 16.5 GPa

| Oxides, wt % | | | | Cations | | |
|------------------------------------|------------------|--------|---------------------------------|---------|-------|-------|
| MgO | SiO ₂ | Total | MgSiO ₃ ^a | Mg | Si | Total |
| <i>Clinoenstatite^b</i> | | | | | | |
| 40.12 | 59.97 | 100.09 | | 1.996 | 2.002 | 3.998 |
| <i>Majorite^c</i> | | | | | | |
| 40.13 | 60.19 | 100.32 | | 1.992 | 2.004 | 3.996 |
| <i>Beta Phase^d</i> | | | | | | |
| 56.61 | 42.81 | 99.42 | | 1.985 | 1.007 | 2.992 |
| <i>Quenched Liquid^e</i> | | | | | | |
| 44.45 | 55.48 | 99.93 | 74.72 | | | |
| 48.32 | 51.22 | 99.54 | 51.03 | | | |
| <i>Quenched Liquid^f</i> | | | | | | |
| 45.77 | 53.99 | 99.76 | 66.56 | | | |

^aNormalized to 100% $\text{MgSiO}_3 + \text{Mg}_2\text{SiO}_4$.

^bCold end of sample, average of three analyses, cations/6 oxygens.

^cHot 2/3 of sample, average of seven analyses, cations/6 oxygens.

^dInclusions in majorite, average of five analyses, cations/4 oxygens.

^eHot end of sample, extreme values of 26 spot analyses.

^fHot end of sample, average of 26 spot analyses.

Therefore, the eutectic liquid composition lies toward MgSiO_3 from this bulk composition. The beta phase-forsterite boundary separates forsterite in the hot zone of the capsule from beta phase in the cooler parts. The boundary lies at a temperature only slightly below that of the eutectic but is irregular and conforms only approximately to an isotherm. Because of this irregularity, beta phase locally extends into the hot zone sufficiently to be in direct contact with the quenched liquid region of the capsule. This irregularity shows that the beta phase-forsterite boundary in the capsule is not strictly an equilibrium feature. However, the temperature of the boundary in this experiment is consistent with a linear extrapolation of the beta phase-forsterite transition at lower temperatures determined by *Katsura and Ito* [1989]. Therefore, the boundary is probably very close to its equilibrium position.

The average of 31 spot analyses of the quenched liquid region of the run on 40En (Table 4 and Figure 5, point B) is very close to the average quenched liquid composition in the run on 80En (Table 3 and Figure 5, point A). Because the two starting compositions lie on opposite sides of the eutectic, the near coincidence of the two liquid compositions indicates that they both lie very close to the eutectic. In Figure 5, the eutectic has been placed between the two liquid compositions at 34 wt % Mg_2SiO_4 , 66 wt % MgSiO_3 . An experiment on the composition 40 wt % Mg_2SiO_4 , 60 wt % MgSiO_3 , carried out by one of us (D. C. Presnall) at The University of Alberta, Canada, shows forsterite as the primary phase, which confirms that the eutectic lies slightly to the MgSiO_3 side of this starting composition. The experiment will be described in detail elsewhere.

Tables 2, 3, and 4 show analyses of periclase, beta phase, clinoenstatite, and majorite. Within the precision of the analyses, solid solution is absent in all of these phases.

TABLE 4. Compositions of Phases From the Experiment on 40En at 2200°C (Nominal) and 16.5 GPa

| Oxides, wt % | | | | Cations | | |
|------------------------------------|------------------|--------|--------------------|---------|-------|-------|
| MgO | SiO ₂ | Total | MgSiO_3^a | Mg | Si | Total |
| <i>Clinoenstatite^b</i> | | | | | | |
| 40.26 | 59.35 | 99.61 | | 2.015 | 1.993 | 4.008 |
| <i>Majorite^c</i> | | | | | | |
| 40.46 | 59.66 | 100.12 | | 2.014 | 1.993 | 4.007 |
| <i>Beta Phase^d</i> | | | | | | |
| 57.47 | 42.47 | 99.94 | | 1.985 | 1.007 | 2.992 |
| <i>Quenched Liquid^e</i> | | | | | | |
| 43.46 | 56.02 | 99.48 | 79.35 | | | |
| 48.56 | 50.93 | 99.49 | 47.14 | | | |
| <i>Quenched Liquid^f</i> | | | | | | |
| 45.99 | 53.57 | 99.56 | 64.74 | | | |

^aNormalized to 100% $\text{MgSiO}_3 + \text{Mg}_2\text{SiO}_4$.

^bCold end of sample, average of two analyses, cations/6 oxygens.

^cAverage of five analyses, cations/6 oxygens.

^dHot 2/3 of sample, average of eight analyses, cations/4 oxygens.

^eHot end of sample, extreme values of 31 spot analyses.

^fHot end of sample, average of 31 spot analyses.

ORIGIN OF THE MANTLE

Herzberg and O'Hara [1985] and *Takahashi* [1986] have argued that the composition of the upper mantle is controlled by a eutectic-like melting process in which the upper mantle is an ultramafic partial melt of the whole mantle. In support of a

eutectic melt origin for the upper mantle, *Scarfe and Takahashi* [1986] and *Takahashi and Scarfe* [1985] found at 16 GPa that the liquidus and solidus of peridotite partially converge to a melting interval of about 100°–150°C. Because complete convergence does not occur, a eutectic in the rigorous sense is not indicated. *Herzberg and O'Hara* [1985] noted that for a multicomponent system with few phases, a true eutectic would not occur, so they referred to the situation in which the solidus and liquidus approach closely as "eutectic-like". In further support of the eutectic melting model, *Takahashi* [1986] and *Ito and Takahashi* [1987] showed that peridotite lies on the olivine-majorite liquidus boundary at about 16 GPa. On the basis of these results and the knowledge from many low pressure studies [e.g., *Chen and Presnall*, 1975] that the forsterite-enstatite eutectic moves toward forsterite as pressure increases, *Takahashi* [1986], *Herzberg et al.* [1988], and *Herzberg and Ohtani* [1988] estimated the position of the forsterite-majorite eutectic in the Mg_2SiO_4 - MgSiO_3 binary system. *Herzberg and O'Hara* [1985] had also proposed a phase diagram indicating their preferred location for the forsterite-majorite eutectic at 15 GPa but no constraining experimental data at 15 GPa existed at that time. These three estimates for the location of the forsterite-majorite eutectic are shown in Figure 5, and it can be seen that they are all highly enriched in forsterite, as are mantle peridotites, in comparison to the determined position of the eutectic.

Our results show that the rate of migration of the forsterite-enstatite eutectic toward forsterite with pressure decreases sharply as pressure increases, in agreement with the results of *Kato and Kumazawa* [1985b, 1986a]. Even though the melting temperature of forsterite is lower than that of majorite at 16.5 GPa (Figure 5), the position of the forsterite-majorite eutectic is inhibited from migrating toward forsterite by expansion of the primary phase fields of AnhB and periclase.

Because more than 80% of the composition of the mantle consists of just the two oxides, MgO and SiO_2 , we argue that the location of the binary eutectic is relevant to the mantle, at least in an approximate way. Therefore, the low forsterite content of the eutectic at 16.5 GPa appears to be inconsistent with formation of the upper mantle as a eutectic-like liquid near this pressure. *Herzberg et al.* [this issue] also reject the eutectic melt model. They propose a two-stage process involving the generation of partial melts that are peridotitic but enriched in silica followed by fractionation of these siliceous peridotite melts at high pressures to generate observed mantle peridotite compositions. They resolve the discrepancy between the location of our binary eutectic liquid composition and that inferred from melting experiments on more complex compositions by drawing the olivine-majorite liquidus boundary so that its Mg/Si ratio increases sharply as the boundary line extends from the binary system to the composition field of peridotites (see their Figure 24). At atmospheric pressure, addition of modest amounts of FeO , CaO , and Al_2O_3 to the system MgO - SiO_2 has only a small effect on the Mg/Si ratio of liquids on the olivine-enstatite boundary [*Bowen*, 1914; *Andersen*, 1915; *Bowen and Schairer*, 1935]. Furthermore, pressures at least up to 3 GPa do not alter this relationship [*Presnall et al.*, 1979; *Sen and Presnall*, 1984; *Milholland and Presnall*, 1989; *Liu and Presnall*, 1990]. Thus, the orientation of the beta phase-majorite liquidus boundary of *Herzberg et al.* [this issue] at 16.5 GPa would not be predicted from data at lower pressures. Further experimental studies are needed to clarify these important liquidus phase relationships.

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