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Experimentally determined postspinel transformation boundary in Mg₂SiO₄ using MgO as an internal pressure standard and its geophysical implications

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[1] We have determined the postspinel transformation boundary in Mg₂SiO₄ by combining quench technique with in situ pressure measurements, using multiple internal pressure standards including Au, MgO, and Pt. The experimentally determined boundary is in general agreement with previous in situ measurements in which the Au scale of Anderson *et al.* [1989] was used to calculate pressure: Using this pressure scale, it occurs at significantly lower pressures compared to that corresponding to the 660-km seismic discontinuity. In this study, we also report new experimental data on the transformation boundary determined using MgO as an internal standard. The results show that the transition boundary is located at pressures close to the 660-km discontinuity using the MgO pressure scale of Speziale *et al.* [2001] and can be represented by a linear equation, $P(\text{GPa}) = 25.12 - 0.0013T(^{\circ}\text{C})$. The Clapeyron slope for the postspinel transition boundary is precisely determined and is significantly less negative than previous estimates. Our results, based on the MgO pressure scale, support the conventional hypothesis that the postspinel transformation is responsible for the observed 660-km seismic discontinuity.

INDEX TERMS: 3630 Mineralogy and Petrology: Experimental mineralogy and petrology; 3954 Mineral Physics: X ray, neutron, and electron spectroscopy and diffraction; 3924 Mineral Physics: High-pressure behavior; 7207 Seismology: Core and mantle; 8124 Tectonophysics: Earth's interior—composition and state (1212); **KEYWORDS:** phase transformation, 660-km discontinuity, in situ X-ray diffraction

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1. Introduction

[2] Seismic discontinuities in the Earth's interior are major features observed by geophysicists. The interpretation of these discontinuities relies on laboratory experimental data at high pressures and temperatures. The postspinel transfor-

mation (spinel = perovskite + sse) in olivine is believed to be responsible for the observed 660-km seismic velocity discontinuity in the mantle. Ito and Takahashi [1989] determined the postspinel transformation boundary in Mg₂SiO₄ by the quench method using a multianvil apparatus. Their experimentally determined boundary coincided with the depth of the 660-km discontinuity at about 1600°C with a negative Clapeyron slope of $-0.0028 \text{ GPa}/^{\circ}\text{C}$. This boundary is widely cited in the literature for interpreting the observed 660-km discontinuity and for pressure calibration in different laboratories around the world. At the time when the boundary was determined, pressure determination in the multianvil apparatus was estimated based primarily on a calibration curve at room temperature. The highest pressure point used in these calibrations was the transition pressure in GaP at 23 GPa and room temperature. The evaluation of temperature effects on the pressure calibration curves is rather empirical without much solid ground.

[3] Recent advances in synchrotron radiation and large-volume cubic apparatus, especially at SPring-8 in Japan, have allowed experimentalists to determine phase boundaries at pressures greater than 14 GPa and high temperature by in situ X-ray diffraction measurements. Irifune *et al.*

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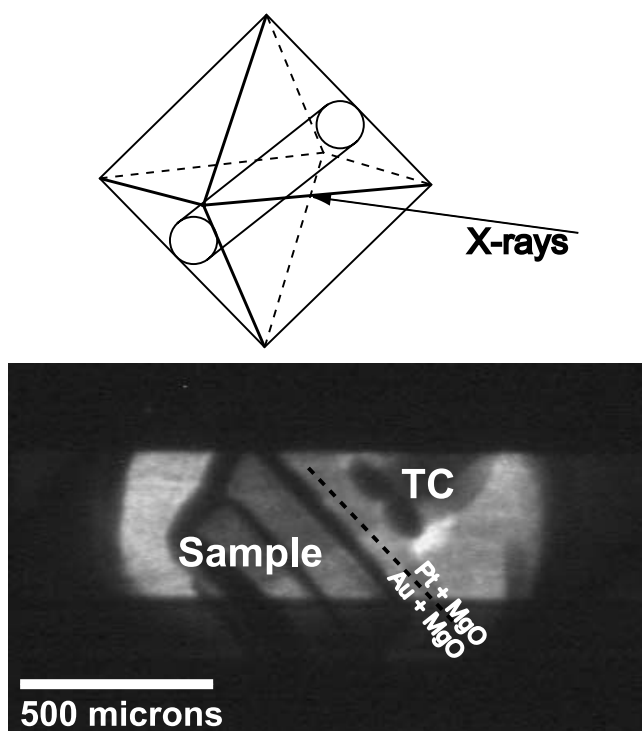


Figure 1. (bottom) X-ray radiograph image of the sample chamber at high pressure and temperature. Multiple pressure standards and samples were loaded in a single sample chamber. (top) Incident X-ray beam in relation to the Re heater in the MgO octahedral pressure medium. See color version of this figure in the HTML.

[1998] redetermined the postspinel transformation boundary in Mg_2SiO_4 by in situ X-ray diffraction measurements in the multianvil apparatus at SPring-8. Their results indicated that the transition pressure of the postspinel reaction in Mg_2SiO_4 was 21.1 GPa at 1600°C, which is about 2 GPa lower than earlier estimates in the conventional quench experiments [e.g., Ito and Takahashi, 1989], although the Clapeyron slope of the boundary is the same as that of Ito and Takahashi [1989]. The pressures in their experiments were determined by measuring sample temperature and the lattice parameter of gold (Au), based on the P - V - T equation of state proposed by Anderson *et al.* [1989].

[4] The in situ measurements by Irifune *et al.* [1998] cast some doubts on the accuracy of the experimentally determined postspinel transformation boundary in Mg_2SiO_4 and stimulated an intense debate on the reliability of the P - V - T equation of state of Au derived from shock compression and thermodynamic data. Chudinovskikh and Boehler [2001] and Shim *et al.* [2001] investigated the postspinel transformation in Mg_2SiO_4 by the laser-heated diamond anvil cell technique with different methods of pressure determination (ruby pressure scale and Pt internal pressure standard, respectively). They concluded that the transformation boundary is generally consistent with that of Ito and Takahashi [1989] by the quenching method, although the accuracy and precision in their pressure determinations have not been fully proven.

[5] Very recently, Katsura *et al.* [2003] reexamined the postspinel transformation boundary in Mg_2SiO_4 using a

technique similar to that used by Irifune *et al.* [1998] but with more rigorous evaluation of the kinetics of the transformation. Their boundary agrees with that of Irifune *et al.* [1998] at 1300°C, but with a much smaller negative Clapeyron slope ($-0.0004 \text{ GPa}/^\circ\text{C}$). A gold internal standard was used in both studies and pressures at high temperature were calculated using the P - V - T equation of state of gold proposed by Anderson *et al.* [1989].

[6] In this study, we present new data on the postspinel transformation boundary in Mg_2SiO_4 using multiple internal pressure standards including Au, MgO , and Pt. Our results provide new insight into the uncertainties in pressure determination at high temperature and the nature of the 660-km seismic discontinuity.

2. Experimental Procedure

[7] The experiments were conducted at the BL04B1 high-pressure and high-temperature beam line in the SPring-8 facility (Japan). A 1500-t hydraulic press with a MA8 double-stage system was used to generate pressure. The second-stage assembly consists of eight corner-truncated tungsten carbide (WC) cubes that form an octahedral cavity for the cell assembly. The synchrotron X-ray beam has access to the sample through the gap between the WC cubes. A detailed description of the facility was given by Utsumi *et al.* [1998]. The facility can adopt cell assemblies used in conventional quenching experiments. We used an 8/3 (octahedron edge length/truncated edge length) assembly described by Bertka and Fei [1997] with a minor modification along the X-ray path to maximize the X-ray flux through the sample chamber. The same assembly was used previously for determining the phase transition boundary of $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ [Hirose *et al.*, 2001a]. We used precast Cr-doped MgO octahedra with pyrophyllite gaskets and Re foil heaters with 25- μm thickness. Sample temperature was measured with an axially located W5%Re-W26%Re (type C) thermocouple. Figure 1 shows a representative X-ray radiograph image of the sample chamber. The powdered Mg_2SiO_4 -forsterite starting material was packed around the thermocouple junction, followed by a thin Re disk. The rest of the sample chamber consists of the internal pressure standards, a thin layer of MgSiO_3 -enstatite powder, and a natural spinel lherzolite powder (KLB-1) enclosed in a Re capsule (Figure 1). We kept the entire sample chamber length less than 500 μm to minimize the temperature gradient. The maximum temperature gradient across a 500 μm long sample chamber in our 8/3 assembly was measured to be 30 $^\circ\text{C}$ at 1900 $^\circ\text{C}$ [van Westrenen *et al.*, 2003].

[8] The internal standards used in this study include Au, Pt, Pd, Mo, W, Ag, and MgO . All the metal standards were mixed with ultrapure MgO powder to minimize recrystallization and coarsening of the metal standards at high temperature. The weight ratio of MgO to metal is about 4:1. In each experiment, two metal standards were used, separated by MgO powder to avoid metal alloying (Figure 1). The Au- MgO mixture was used in every experiment to serve as a common standard for comparison.

[9] For each experiment, we pressurized the sample to a targeted oil pressure at room temperature and then heated the sample to a targeted temperature. The sample pressures were continuously monitored by measuring the unit cell

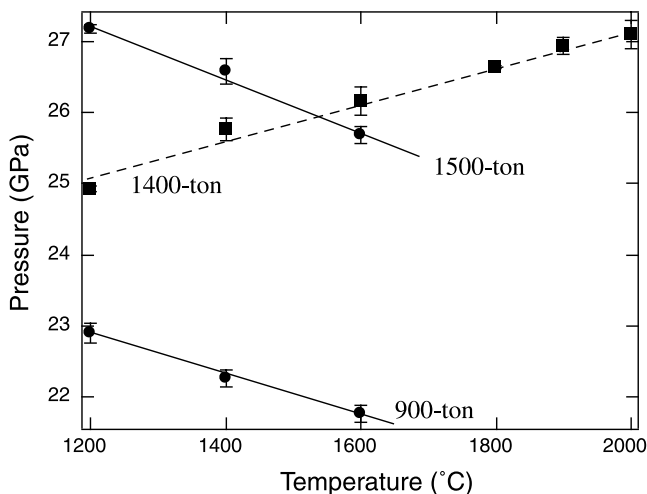


Figure 2. Pressure changes during heating. For our 8/3 assembly, pressure decreases with increasing temperature at given oil pressures (solid circles). However, the temperature dependence may change if the P - T path is changed. We observed that pressure increases with increasing temperature after a temperature cycle at 680 t (solid squares). Pressures were calculated using the Au scale of *Anderson et al.* [1989].

parameters of the internal standards, using the energy-dispersive X-ray diffraction technique. The diffraction data were collected with a single-element (Ge) solid-state detector, at a fixed 2θ angle. The energy channel number relationship was determined by measuring the energies of well-determined X-ray emission lines (K_{α} and K_{β}) of Cu, Mo, Ag, Ta, Pt, Au, Pb, and gamma radiation from ^{133}Ba , ^{109}Cd , ^{152}Eu , and ^{57}Co . The 2θ angle was calibrated by measuring the energies of diffraction peaks, corresponding to the known interplanar spacings d_{hkl} , of gold (Au) at ambient conditions with $a_0 = 4.0782$ Å. We typically set 2θ angle at around 5.8° . The measured unit cell parameters for MgO and Pt at ambient conditions are 4.2118(5) and 3.9231(5) Å, respectively. The diffraction lines of (111), (200), (220), and (311) typically were used to derive the unit cell parameters. Typical beam size used for the high-pressure diffraction measurements was 50×100 μm . With the X-ray image system, it was relatively easy to locate the pressure standards and determine the relative position of the diffraction spot to the thermocouple (Figure 1).

[10] All the phases involved in the postspinel transformation from Mg_2SiO_4 -spinel (ringwoodite) to $MgSiO_3$ -perovskite plus MgO-periclase can be quenched to ambient conditions. In situ observations of the transformation boundary would seem redundant, except that some of the transformations are inhibited by sluggish kinetics, as discussed by *Katsura et al.* [2003]. In the previous multianvil studies by in situ X-ray diffraction [*Irfune et al.*, 1998; *Katsura et al.*, 2003], the transformation boundary was continuously measured by X-ray diffraction while the pressures were determined from the internal standard. This method has the advantage of collecting many data points across the phase boundary in a single experiment. However, the procedure is complicated by the difficulty of positively identifying the phases present from the diffraction data, by

the sluggish kinetics of the transformation, and by recrystallization at high temperatures. The discrepancy between the results of *Irfune et al.* [1998] and *Katsura et al.* [2003] may result from the differences in experimental procedure and in dealing with the kinetics of the transformation.

[11] In this study, we adopted a different strategy for determining the phase equilibrium boundary. The experiments were performed in the quench experiment fashion, with each experiment held at the desired P - T condition for at least 2 hours. During each experiment we continuously monitored the pressure of the sample by collecting in situ measurements on the internal pressure standards. Using this procedure, we could only obtain one data point for each experiment that could be used to map the phase boundary. However, this point provides a definitive answer regarding the stable phase assemblage at that P - T condition. In addition, our strategy provides valuable information about the run history that is useful for understanding the behavior of multianvil assemblies at high pressure and temperature. Figure 2 shows the effect of temperature on pressure for a given load (oil pressure) for three representative runs. We observed that pressure usually decreases with increasing temperature, whereas pressure increased in some experiments with an identical cell assembly, but different P - T paths. The temperature dependence of pressure is a complex function of thermal pressure and material relaxation, and depends on the P - T path of the run. Figure 3 shows the time dependence of pressure at a given oil pressure and temperature condition for three typical runs, all conducted at similar conditions of about 22 GPa and 1873 K. Pressure generally drops about 0.5 GPa in the first 30–60 min and then becomes stable. Pressures used to constrain the phase boundaries reported in this study are the final pressures before quenching (usually after 2 hours).

[12] After quenching, longitudinal sections of the experimental charges were mounted and polished. Chemical composition maps and quantitative chemical analyses were obtained with a JEOL-SUPERPROBE JXA-8900 electron

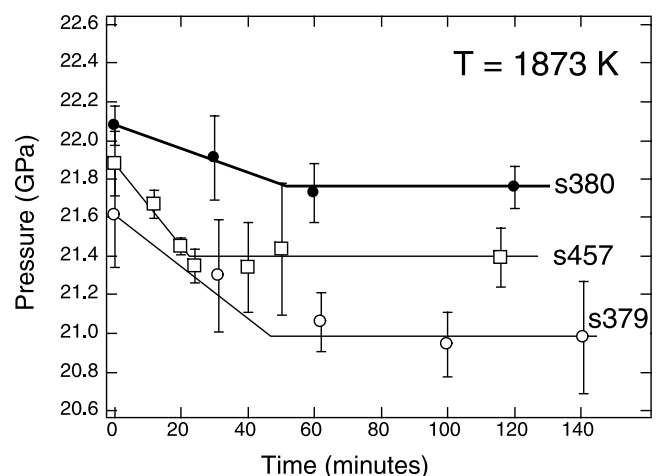


Figure 3. Time dependence of pressure at high pressure and temperature for three representative runs, s380 (solid circles), s457 (open squares), and s379 (open circles). At constant oil pressure and 1873 K, sample pressure relaxation occurs at the first 30–60 min. Typical pressure drop is ~ 0.5 GPa during the relaxation.

Table 1. Experimental P - T Conditions and Run Products^a

Run	T , K	Standards	a_{Au} , Å	P_{Au} , ^b GPa	a_{MgO} , Å	P_{MgO} , ^c GPa	a_{Pt} , Å	P_{Pt} , ^d GPa	Mg_2SiO_4	MgSiO_3
s460	1673	Au + MgO + Pd	3.9902(12)	21.89(20)	4.1041(18)	23.43(25)			Pv + MgO/Rw	Pv
s695	1673	Au + MgO + Pt	3.9823(7)	23.22(13)	4.0972(9)	24.56(15)	3.8606(14)	24.34(39)	Pv + MgO	Pv
s379	1873	Au + MgO + Pt	4.0040(19)	20.98(29)	4.1208(36)	22.13(53)	3.8770(1)	21.44(3)	Rw	
s455	1873	Au + MgO + Pd	4.0050(3)	20.83(5)	4.1208(15)	22.13(22)			Rw	Ak
s696	1873	Au + MgO + Pt	4.0044(15)	20.91(23)	4.1174(10)	22.66(15)	3.8814(10)	20.35(24)	Rw	Pv
s457	1873	Au + MgO + Ag	4.0013(9)	21.39(15)	4.1190(38)	22.41(59)			Rw	Pv
s380	1873	Au + MgO + Pt	3.9989(7)	21.76(11)	4.1149(20)	23.06(30)	3.8750(13)	21.95(32)	Pv + MgO	
s451	1873	Au + MgO + Mo	3.9830(6)	24.35(10)	4.0995(27)	25.56(43)			Pv + MgO	
s454	2023	Au + MgO + W	4.0101(14)	21.03(22)	4.1244(6)	22.60(9)			Rw	
s700	2023	Au + MgO	4.0058(22)	21.68(34)	4.1218(10)	23.00(15)			Pv + MgO	
s459	2173	Au + MgO + Pt	4.0177(6)	20.91(9)	4.1380(20)	21.56(28)	3.8895(6)	20.47(14)	Wa	Pv
s453	2173	Au + MgO + Mo	4.0148(7)	21.33(11)	4.1320(15)	22.46(21)			Wa	Pv
s694	2173	Au + MgO + Pt	4.0138(8)	21.47(13)	4.1296(26)	22.82(37)	3.8821(10)	22.26(25)	Pv + MgO/Rw/Wa	Pv

^aValues in parentheses are standard deviations. Abbreviations are Pv, perovskite; Rw, ringwoodite (spinel); Wa, wadsleyite (β phase); and Ak, Akimotoite (ilmenite).

^bPressures were calculated using the Au scale of *Anderson et al.* [1989] with $a_0 = 4.0782(2)$ Å.

^cPressures were calculated using the MgO scale of *Speziale et al.* [2001] with $a_0 = 4.2118(5)$ Å.

^dPressures were calculated using the Pt scale of *Holmes et al.* [1989] with $a_0 = 3.9231(5)$ Å.

microprobe. The quenched phases were identified with micro-Raman spectroscopy and from the X-ray composition maps. The existing Raman spectra of Mg_2SiO_4 -spinel (ringwoodite), Mg_2SiO_4 -wadsleyite, MgSiO_3 -ilmenite (akimotoite), and MgSiO_3 -perovskite were used as fingerprints to identify the phase assemblages in the quenched samples [*Bertka and Fei, 1997*].

3. Experimental Results

[13] We conducted 13 multianvil experiments at the SPring-8 synchrotron facility in the temperature range 1673–2173 K. The results are summarized in Table 1. At each temperature the phase boundary was tightly bracketed by multiple runs at different pressures. Au and MgO were used as the internal pressure standards in all the experiments. A third standard (Pt, Mo, W, Pd, or Ag) was also used in some experiments for comparison. Table 1 also lists the unit cell parameters of Au and MgO for each experiment, which were derived from the diffraction data collected right before the runs were quenched. The corresponding pressures were calculated using the equations of state for Au proposed by *Anderson et al.* [1989] and for MgO by *Speziale et al.* [2001]. Six out of the 13 experiments also contained Pt as a pressure standard. The pressures calculated from the equation of state of Pt [*Holmes et al., 1989*] are also listed in Table 1. Other pressure standards such as Pd, Ag, Mo, and W did not yield useful data at temperatures above 1873 K because of either melting or reaction with MgO. Useful data for these standards were obtained at relatively low temperatures (<1673K) and are discussed elsewhere [*Fei et al., 2003*].

[14] The Mg_2SiO_4 -forsterite starting material was transformed into either Mg_2SiO_4 -polymorphs (ringwoodite or wadsleyite) or the MgSiO_3 -perovskite plus MgO assemblage at high pressure and temperature. In run s460 ($T = 1673\text{K}$), we observed ringwoodite (Mg_2SiO_4 -spinel) in the center (colder area in the radial temperature distribution) and the MgSiO_3 -perovskite plus MgO assemblage near the heater (hotter zone) in the same quenched charge, indicating that the P - T condition was very close to the phase boundary. In experiments at 2173 K, we observed wadsleyite (β phase), replacing ringwoodite. In run s694, we observed both

wadsleyite and the MgSiO_3 -perovskite plus MgO assemblage in the hot zone. A small amount of ringwoodite was also found in the coldest area in this charge, indicating that this run was near the triple point. The fact that wadsleyite was found in the hottest zone of the charge indicates that the phase boundary between wadsleyite and MgSiO_3 -perovskite plus MgO has a positive Clapeyron P - T slope. Figure 4 shows the phase diagram of Mg_2SiO_4 using the Au pressure scale by *Anderson et al.* [1989]. The slope of the postspinel transformation boundary is tightly constrained from the runs at 1673 K and 2173 K. This data set yielded a negative slope of -0.0008 GPa/K, but less negative than that determined by *Irifune et al.* [1998]. Our result is in a good agreement with that of *Irifune et al.* [1998] at relatively low temperature (e.g., 1573 K). The difference in transition pressures becomes significant at higher temperatures (e.g., about 1 GPa difference at 2073 K). Our data are in remarkable agreement with those of *Katsura et al.* [2003] in both transition pressures and Clapeyron P - T slope, even though our experimental strategies differed substantially.

[15] Phases present in our experiments were identified after quenching with micro-Raman spectroscopy [*Bertka and Fei, 1997*], which is extremely effective with high spatial resolution (1 μm). The P - T history for each run is carefully documented by monitoring the unit cell parameters of the internal pressure standards as a function of temperature and time. As shown in Figures 2 and 3, pressure relaxation was observed with increasing temperature and there is an ~ 0.5 -GPa pressure drop in the first 30–60 min after target run temperature was reached. Experiments conducted in this study usually went to higher pressure initially and then relaxed to the reported pressures. Possible metastable survival of phase assemblages established during the early heating of the experiments was a concern. After the sample had relaxed at run temperature, we always maintained the sample at constant pressure for at least 60 min (Figure 3). Of the 13 experiments conducted in this study, we observed mixed phase assemblages in only two runs (s460 and s694). By being able to determine the spatial distribution of the coexisting phases in the quenched run product we can clearly show that the coexistence of the low- and high-pressure assemblages is most probably caused by a

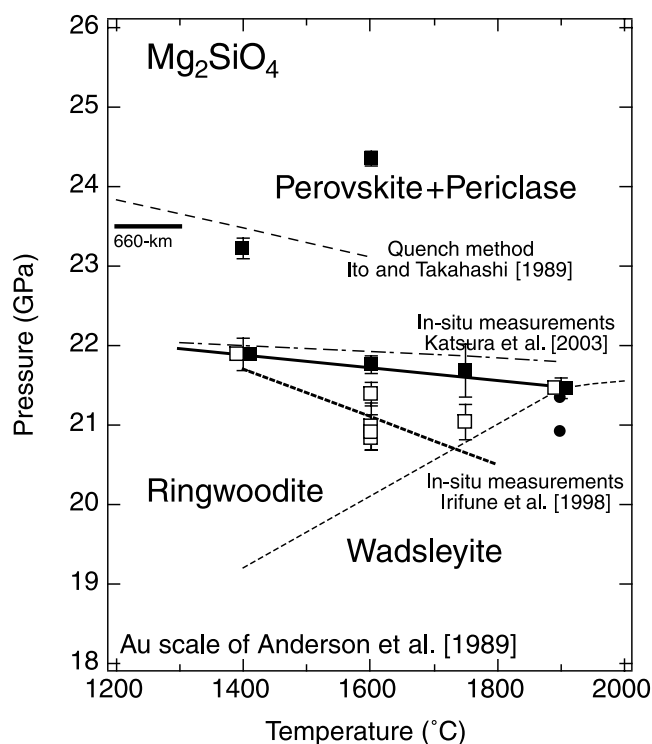


Figure 4. Phase boundary of the postspinel transformation in Mg_2SiO_4 , using the Au scale of Anderson *et al.* [1989] (solid line). The open and solid squares represent conditions where ringwoodite or perovskite + periclase, respectively, were stable. Wadsleyite was observed at 1900°C (solid circles). Boundaries determined by Ito and Takahashi [1989] (dashed line), by Irifune *et al.* [1998] (dotted line), and by Katsura *et al.* [2003] (dot-dashed line) were also plotted for comparison.

small temperature gradient at a pressure near the phase boundary. The survival of metastable phase assemblages is not consistent with the observations that two runs with almost identical P - T path and history (compare Figure 3) produced different phase assemblages with just a small pressure difference (compare runs s457 and s380 at 1600°C; runs s454 and s700 at 1750°C; runs s453 and s694 at 1900°C). For example, the perovskite phase assemblage was probably produced during the early heating in experiments s457 and s380. However, the final phase assemblages are ringwoodite for s457 and perovskite + periclase for s380, respectively, with the final pressure of s380 only 0.37 GPa higher than that of s457 (Figure 3). Although we did not take in situ measurements of the diffraction patterns of the sample, our results are remarkably similar to those reported using in situ measurements by Katsura *et al.* [2003] who also made in situ X-ray observations on the sample itself during heating.

[16] All three multianvil studies [Irifune *et al.*, 1998; Katsura *et al.*, 2003; this study], based on the Au pressure scale by Anderson *et al.* [1989], lead to the conclusion that the postspinel transformation boundary determined by in situ measurements is about 1.5–2.0 GPa lower in pressure than previously determined by quench method [e.g., Ito and Takahashi, 1989]. This conclusion would have pro-

found implications for the nature of the 660-km seismic discontinuity.

[17] It seems that the results from the in situ measurements are robust, since they have been reproduced by three independent studies. In particular, there is a remarkable agreement between our study with exceptionally long run duration and that of Katsura *et al.* [2003], who carefully examined the kinetics of the transformation. The discrepancy between the in situ measurements and quench method could result from the uncertainties in pressure determination at high temperature. In this study, we further examined the phase boundary using two alternative pressure standards (MgO and Pt) in addition to Au. Figure 5 shows the phase diagram of Mg_2SiO_4 based on the MgO pressure scale by Speziale *et al.* [2001]. The phase boundary determined from the MgO scale occurs at higher pressures than that from the Au scale of Anderson *et al.* [1989] and is in general agreement with the boundary determined from quench experiments by Ito and Takahashi [1989]. It has a negative slope of -0.0013 GPa/K, slightly more negative than the slope determined using Au as the pressure standard (-0.0008 GPa/K) but still less negative than that of Ito and Takahashi [1989] (-0.0028 GPa/K).

[18] In several experiments, we also used Pt as an internal pressure standard (Table 1). The pressures calculated from the Pt scale of Holmes *et al.* [1989] are generally lower than those from the MgO scale of Speziale *et al.* [2001] by about

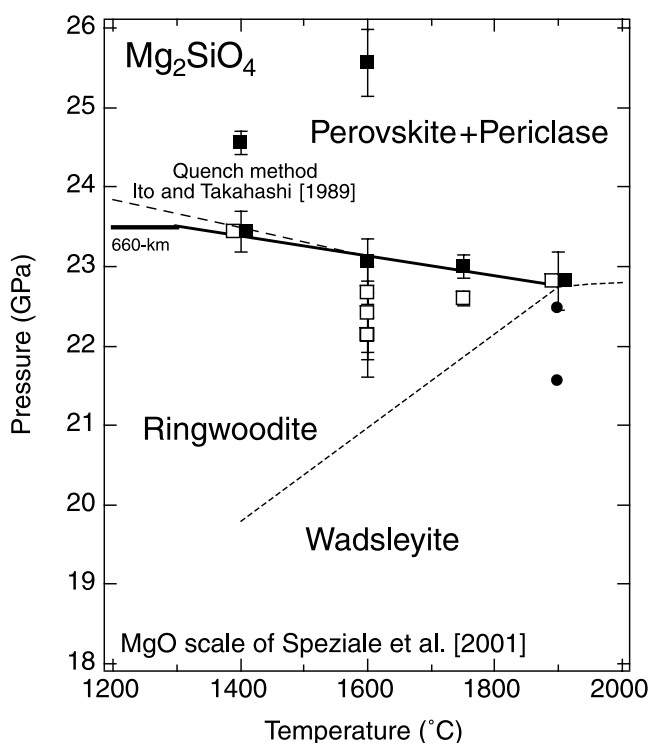


Figure 5. Phase boundary of the postspinel transformation in Mg_2SiO_4 , using the MgO scale of Speziale *et al.* [2001] (solid line). The open and solid squares represent conditions where ringwoodite or perovskite + periclase, respectively, were stable. Wadsleyite was observed at 1900°C (solid circles). Boundary determined by Ito and Takahashi [1989] (dashed line) was also plotted for comparison.

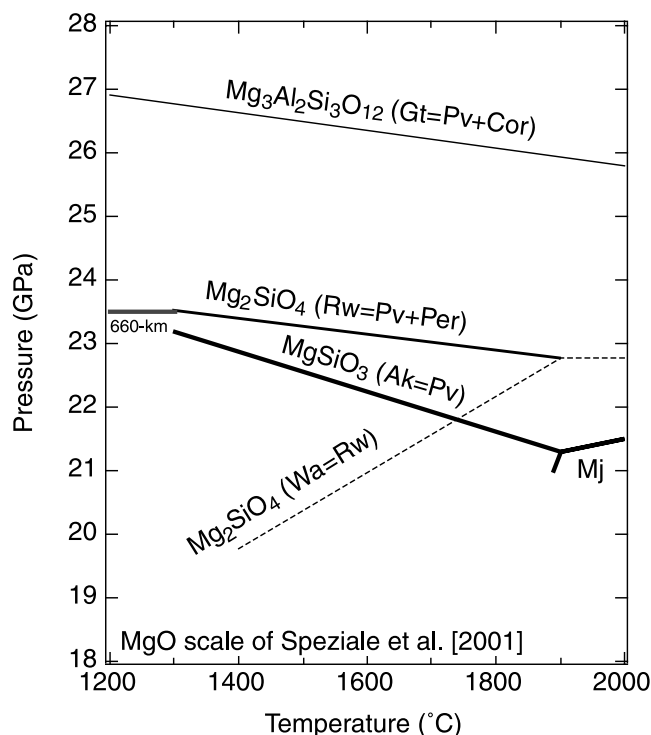


Figure 6. Phase boundaries for the pyrope-perovskite + corundum (thin line), ringwoodite-perovskite + periclase (thick line), and akimotoite-perovskite (heavy line) transformations. The pyrope-perovskite + corundum phase boundary in $Mg_3Al_2Si_3O_{12}$ by Hirose *et al.* [2001a] and the akimotoite-perovskite phase boundary in $MgSiO_3$ by Hirose *et al.* [2001b] were corrected to be consistent with the MgO scale of Speziale *et al.* [2001]. Abbreviations are Gt, garnet; Pv, perovskite; Cor, corundum; Rw, ringwoodite; Per, periclase; Wa, wadsleyite; and Mj, majorite.

1.5 GPa. Although there are not enough data to construct a well-defined phase boundary using the Pt standard, the available data points indicate a similar phase boundary as using the Au standard.

[19] Shim *et al.* [2001] reported that the postspinel transformation in Mg_2SiO_4 occurs at ~ 24 GPa, consistent with the depth of 660km, using the Pt scale. Our results based on the Pt standard indicate that the discrepancy between the multianvil results [Irifune *et al.*, 1998; Katsura *et al.*, 2003; this study] and the results from laser-heating experiments in the diamond anvil cell [Shim *et al.*, 2001] cannot be explained by the difference between the Pt and Au scales. It is probably caused by different experimental procedures and techniques. Further experiments are required to resolve the discrepancy.

[20] In addition to using Mg_2SiO_4 -forsterite as the starting material, we also loaded a thin layer of $MgSiO_3$ -enstatite powder in several experiments to examine the akimotoite (ilmenite)-perovskite phase boundary in $MgSiO_3$. We observed akimotoite only in run s455 at 1600°C and 20.83 GPa (Au scale of Anderson *et al.* [1989]) and $MgSiO_3$ -perovskite is the stable phase in all other runs (Table 1). The transition pressure for the akimotoite-perovskite phase boundary at 1600°C is tightly constrained at a pressure between 20.83 and 20.91 GPa by runs

s455 and s696. This result is in excellent agreement with that of Hirose *et al.* [2001b], who determined the majorite-akimotoite-perovskite phase boundaries in $MgSiO_3$ by in situ measurements.

4. Discussion

[21] It is not unexpected that the use of different internal pressure standards will result in significant differences in the position of the phase boundaries (compare Figures 4 and 5) because the existing equations of state of pressure standards (Au, MgO, and Pt) predict pressures that can differ by as much as 3 GPa at conditions corresponding to the 660-km seismic discontinuity [e.g., Shim *et al.*, 2002; Fei *et al.*, 2003]. Fei *et al.* [2003] compared pressures calculated from different equations of state of Au, MgO and Pt in the same experiment and found that the Au scale of Jamieson *et al.* [1982] gave the highest pressure whereas the MgO scale of Jamieson *et al.* [1982] predicted the lowest pressure. The pressures calculated from the Au scale of Shim *et al.* [2002] are about 0.5 GPa lower than those from the MgO scale of Speziale *et al.* [2001] at temperatures between 1473 and 2173 K. At the present time, it is difficult to judge which pressure scale predicts the correct pressures at high temperatures. With the lack of an absolute pressure scale, it is important to choose a reference pressure scale for the convenience of interlaboratory comparison and data consistency. Fei *et al.* [2003] argued that the MgO scale of Speziale *et al.* [2001] might be used as such a reference scale because MgO has been extensively studied and its P - V - T data are the least controversial among all pressure standards. The MgO scale of Speziale *et al.* [2001] is also in a good agreement with the results from molecular dynamics simulation of the thermal equation of state of MgO by Matsui *et al.* [2000]. The calculated pressures from these two scales generally agree within 0.25 GPa at mantle temperatures. In addition, the MgO scale is likely to be the first one to be tested by redundant equation-of-state measurements (e.g., simultaneous X-ray diffraction and acoustic measurements) in the near future, which would provide an absolute pressure scale. Zha *et al.* [2000] have already successfully demonstrated that it is possible to measure the volume and elasticity simultaneously at room temperature by combining Brillouin scattering and X-ray diffraction techniques. It is just a matter of time before these measurements are extended to high temperatures. Simultaneous measurements of volume and elasticity by combining ultrasonic and X-ray diffraction techniques are also becoming possible to independently test the MgO scale.

[22] The use of the MgO scale of Speziale *et al.* [2001] as a reference scale is also practical because the existing high-pressure and high-temperature data produced by quenching experiments in the last two decades require only a minimal pressure correction. For the purpose of data consistency, we recalculated the pressures for the majorite-perovskite phase boundary in $Mg_3Al_2Si_3O_{12}$ by Hirose *et al.* [2001a] and the majorite-akimotoite-perovskite phase boundaries in $MgSiO_3$ by Hirose *et al.* [2001b], using the measured pressure differences between the Au and MgO scales [Fei *et al.*, 2003]. Figure 6 shows the phase transition boundaries in Mg_2SiO_4 , $MgSiO_3$, and $Mg_3Al_2Si_3O_{12}$ that are consistent with the MgO scale of

Speziale et al. [2001]. The phase boundaries for the pyrope-perovskite + corundum, ringwoodite-perovskite + periclase, and akimotoite-perovskite transformations can be represented by linear equations, $P(\text{GPa}) = 28.58 - 0.0014T(^{\circ}\text{C})$, $P(\text{GPa}) = 25.12 - 0.0013T(^{\circ}\text{C})$, and $P(\text{GPa}) = 27.27 - 0.0031T(^{\circ}\text{C})$, respectively.

[23] It is known that the akimotoite-perovskite phase transition boundary is located at lower pressures than the postspinel transition boundary [e.g., *Ito and Takahashi*, 1989]. The quench experiments indicate that the two boundaries have similar Clapeyron P - T slopes. Our in situ measurements indicate that the akimotoite-perovskite phase transition boundary has a much more negative slope than the postspinel transition boundary and the two boundaries would cross over at about 1160°C (Figure 6). At temperatures below 1160°C , Mg_2SiO_4 -spinel is expected to transform into the akimotoite (ilmenite) + MgO assemblage rather than the perovskite + MgO assemblage. This result is consistent with thermodynamic analysis of self-consistent database for the Mg_2SiO_4 and $MgSiO_3$ systems [*Fei et al.*, 1990].

[24] While the accuracy in the measured pressures for the postspinel transition boundary is still in doubt because of the uncertainties in the P - V - T equations of state of the pressure standards, the precision (reproducibility) of the phase boundary is high, especially when comparing our result with that of *Katsura et al.* [2003]. Both studies took special care regarding the kinetics of the transformation and obtained remarkably similar results. The typical precision in the measured pressures is about 0.25 GPa, propagated from the uncertainties in the measured unit cell parameters. Uncertainties in temperature could significantly affect the calculated pressures at high temperature. Although we control the experimental temperature to precision within 1 degree, the temperature uncertainties due to the effect of pressure on thermocouple emf are unknown. Several attempts have been made to evaluate the pressure effect on the emf for different types of thermocouples [e.g., *Getting and Kennedy*, 1970; *Mao et al.*, 1971; *Walter et al.*, 1995]. We recently reexamined this effect over a wide pressure and temperature range and concluded that it is possible to underestimate temperature by 100 K at 23 GPa and 2000 K [*Li et al.*, 2003]. An underestimation of temperature by 100 K would lower the calculated pressures by ~ 0.6 GPa.

5. Geophysical Implications

[25] Olivine is the dominant mineral in the upper mantle. With increasing pressure, it transforms to wadsleyite and then to ringwoodite, and finally decomposes into orthorhombic silicate perovskite plus magnesiowüstite. The transition pressures for the olivine-wadsleyite phase transition and ringwoodite-perovskite + magnesiowüstite postspinel transformation are closely associated with the depths of the 410-km and 660-km seismic discontinuities, respectively. In situ measurements of the postspinel transformation boundary in Mg_2SiO_4 clearly demonstrate that the transition pressure is too low to match the depth of the 660-km discontinuity when the Au scale of *Anderson et al.* [1989] is used for pressure determination. The use of improved Au scales of *Shim et al.* [2002] and *Fei et al.*

[2003] reduces the difference. A reasonable match between experiment and observation is obtained when the MgO scale of *Speziale et al.* [2001] is used for pressure determination. By direct measurements using MgO as the internal pressure standard, we, for the first time, demonstrate that it is possible to reconcile the discrepancy between the transition pressure of the postspinel transformation in Mg_2SiO_4 and the depth of the 660-km seismic discontinuity.

[26] The Earth's mantle is a multicomponent chemical system. Compositional effects on the postspinel phase boundary have to be examined before definitive conclusions on the nature of the 660-km discontinuity can be drawn. *Fei et al.* [2002] reported in situ measurements of the postspinel transformation in a natural peridotitic composition (KLB-1). They showed that the transition pressure in the peridotitic composition is about 0.8 GPa lower than that in Mg_2SiO_4 . This compositional effect increases the mismatch between the experimentally determined transition pressure and the depth of the discontinuity. On the other hand, underestimation of experimental temperature due to the effect of pressure on thermocouple emf could help to decrease the difference. The ultimate solution to the problem requires better determination of pressures based on an absolute pressure scale, detailed study of the postspinel transformation in a natural composition, and better understanding of the correction of the measured temperatures at high pressure.

[27] The postspinel phase boundaries in Mg_2SiO_4 determined by using the Au scales of *Fei et al.* [2003] and the MgO scales of *Speziale et al.* [2001] and *Matsui et al.* [2000] agree within 0.3 GPa. Without an absolute pressure scale at high temperature, we can determine pressures at mantle temperature (e.g., 2000 K) within 4% at best. Despite the large uncertainty in determining the absolute pressure, which limits our ability to directly correlate the transition pressure with the depth of the discontinuity, the precision in the relative pressure determination is rather high using in situ measurements. Therefore the Clapeyron slope for the postspinel transition boundary is very well constrained in this study. The best estimate of the Clapeyron slope is $-0.0013(3)$ GPa/K, significantly less negative than previous estimates (around -0.003 GPa/K). A less steep Clapeyron slope implies that the postspinel transition is a less effective barrier to mantle convection. This could have significant implications for mantle dynamics and interpretations of seismic observations.

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