converting to brightness temperatures.
27. Bands were formed by summing the observed radiance over a set of TES spectral points. The dust band used 30 points over 889 to 1196 cm^{-1}, the pair of dust continuum bands consisted of eight points at 772 to 846 cm^{-1} and eight points at 1238 to 1312 cm^{-1}. The surface bands were "red"; eight points at 360 to 434 cm^{-1} and blue, eight points at 1300 to 1376 cm^{-1}. The atmospheric temperature was estimated by summing two bands on each side of the 15 μm CO_2 band corresponding to a weighting function peaked near 3 mbars.
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33. We wish to thank the entire TES engineering team at the Hughes Santa Barbara Research Center, led by S. Silverman and M. Greenfield, and at Arizona State University (ASU), led by G. Mehall. We thank N. Gorelick, K. Bender, S. Anwar, M. Weiss-Malik, J. Bandfield, V. Hamilton, M. Lane, S. Ruff, and K. Qazi at ASU. We thank B. Allen II, L. Fenton, A. Gordon, L. Mazzuca, W. McMillan, S. Mason Jr., K. Walker, and W. Maguire. We thank the Goddard Software Development Team, headed by S. Dason and E. Greene, including J. Guerber, K. Horrocks, M. Kaelberer, C. Martin, R. Thompson, E. Winter. We thank T. Titus and K. Mullins at the U.S. Geological Survey in Flagstaff. Finally, we thank the entire spacecraft and mission operations teams at Jet Propulsion Laboratory and Lockheed Martin.

21 January 1998; accepted 13 February 1998

The Postspinel Phase Boundary in Mg_2SiO_4 Determined by in Situ X-ray Diffraction

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The phase boundary between spinel (γ phase) and $MgSiO_3$ perovskite + MgO periclase in Mg_2SiO_4 was determined by in situ x-ray measurements by a combination of the synchrotron radiation source (SPring-8) and a large multianvil high-pressure apparatus. The boundary was determined at temperatures between 1400° to 1800°C, demonstrating that the postspinel phase boundary has a negative Clapeyron slope as estimated by quench experiments and thermodynamic analyses. The boundary was located at 21.1 (±0.2) gigapascals, at 1600°C, which is ~2 gigapascals lower than earlier estimates based on other high-pressure studies.

Olivine $(Mg, Fe)_2SiO_4$, the most abundant mineral in the upper mantle, transforms to modified spinel and spinel structures at high pressure (~13.5 and ~18 GPa, at 1400° and 1500°C, respectively) and then decomposes into an assemblage of $MgSiO_3$-rich perovskite and (Mg,Fe)O ferro-periclase (at ~23 GPa and 1600°C) (*1*). The olivine–to–modified spinel and the postspinel transformations are believed to underlie the two major seismic discontinuities at 410- and 660-km depths in the mantle, respectively. Previous attempts to estimate the pressure and temperature at which the olivine–to–modified spinel transformation occurs have used quench experiments and thermodynamic analyses (*2*). Only a few experimental studies have tried to define the postspinel phase boundary (*3*, *4*), despite its importance in elucidating the nature of the 660-km discontinuity, chemical composition of the lower mantle, and dynamic processes of the subducting slabs and upwelling mantle plumes. These studies were based on quench experiments in which the pressure was estimated from calibration curves that used the phase boundaries of some reference materials (for example, covalent to metallic in ZnS, GaAs, and GaP; coesite-stishovite in SiO_2; ilmenite-perovskite in $MgSiO_3$). However, the phase boundaries of these materials have not been accurately determined, particularly at pressures above 20 GPa and at high temperatures (1000° to 2000°C) relevant to Earth's interior. Accordingly, there are uncertainties in the pressures at which a phase boundary has been observed in these quench experiments.

Several attempts were made to determine the boundaries of the phase transformations associated with the 410- and 660-km discontinuities by in situ x-ray diffraction measurements under high pressure and temperature (*5*, *6*). These studies combined a synchrotron radiation source with a multianvil apparatus, so that the temperature and pressure were simultaneously measured during the experiment with pressure scales based on the known volume changes of reference materials, such as NaCl and Au, to ensure an accurate determination of the phase boundaries. Using this technique, Morishima *et al.* determined the phase boundary between olivine and modified spinel (*5*). However, the postspinel transformations could not be determined because a single-stage multianvil system could not attain pressures higher than 20 GPa, and the run temperatures were limited to about 1500°C.

A double-stage multianvil system, with eight sintered diamond cubes used as second-stage anvils, was used to observe the ilmenite-perovskite phase boundary in $MgSiO_3$ and the postspinel phase boundary at pressures up to 28 GPa (*6*). In these studies, the uncertainty of the temperature measurement was large (±50° to 200°C), and the run temperature and the heating duration were limited to 1200° to 1300°C and 30 min, respectively, which hindered accurate determination of these phase boundaries.

A new generation synchrotron radiation facility operated at 8 GeV (SPring-8) was constructed in Hyogo prefecture, Japan, and a beamline equipped with a newly designed 1500-ton multianvil apparatus (SPEED-1500) is now available for high-pressure mineral physics studies (*7*). We developed a cell design (Fig. 1) (*8*) suitable for this system and conducted high-pressure and -temperature runs to define the postspinel phase boundary in Mg_2SiO_4 using an in situ x-ray diffraction technique.

We used pure synthetic forsterite (Mg_2SiO_4) starting material crushed and ground in a harden ceramic mortar. The powdered forsterite was mixed with a fine powder of Au (grain size ~1 μm) of 5 volume %, which was used as a pressure reference material (*9*). This mixture was pelletized and sintered in an oven at 950°C for about 12 hours and then transferred to the high-pressure furnace assembly. The whole assembly was dried at 120°C before the high-pressure and -temperature experiment so that the effect of water on the phase transformation was minimized. Pressure was applied first to up to about 28 GPa (*10*), and then the temperature was increased. During this process, x-ray diffraction data were acquired for typically 300 s by an energy-dispersive system (*11*), and the different phases were identified.

We conducted three runs at pressures between 19 to 25 GPa and temperatures be-

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tween 800° to 1800°C. The heating duration was typically 10 to 20 min at each *P-T* condition in which the x-ray data were acquired, yielding total heating durations of 6 to 16 hours under these *P-T* conditions. In the first experiment, S-010, pressure was increased to a range where olivine (Fig. 2A) decomposes to perovskite + periclase at high temperature [~28 GPa (*10*)], and then the temperature was increased while the oil pressure of the apparatus was kept constant. The apparent pressure dropped about 2 to 3 GPa with increasing temperature at the initial stage of heating, and olivine persisted to 900°C, at pressures of about 25 GPa. The transformation of olivine to the spinel phase was then observed at limited temperatures of 1000° to 1100°C at pressures of 23 to 25 GPa (Fig. 2B). The occurrence of the spinel phase under these conditions is presumably caused by the metastable growth of this phase (*12*), because we observed rapid crystallization of perovskite and periclase at 1100°C after 5 to 10 min. Most of the metastable spinel was converted to perovskite and periclase at 1200°C within a few minutes, and the diffraction peaks of spinel completely disappeared after 20 min of heating. When the temperature reached 1500°C in the postspinel-phase field (Fig. 2C), temperature was decreased slowly to 1400°C, where the appearance of the spinel phase was confirmed [arrow (1), Fig. 3]. Thus, we observed the perovskite + periclase to spinel transformation between these temperatures at pressures near 21.5 GPa (Fig. 3). We then gradually increased the temperature again (for example, Fig. 2D) up to 1600°C, where pressure dropped to 20.9 GPa, and no further transformation was observed under such conditions for about 60 min.

In the second experiment (S-011), we synthesized the spinel phase at relatively low pressure and temperature (~21.5 GPa, 1250°C) and attempted to constrain the phase boundary by slowly increasing the pressure up to 22.2 GPa while temperature was maintained at 1250°C. However, we were unable to detect the formation of perovskite and periclase. We observed some changes of the relative intensities of the diffraction peaks of spinel, but this may be attributed to grain growth of spinel under these conditions.

In the third experiment (S-012), we synthesized the assemblage of perovskite + periclase from the metastably grown spinel phase at pressures of 22 to 23 GPa and at temperatures 1200° to 1500°C, at a fixed oil pressure. Temperature was then increased from 1500° to 1600°C in about 30 s and then slowly (~10°C per minute) decreased until the occurrence of the diffraction peaks of spinel was confirmed. We observed the partial transformation of perovskite + periclase back to spinel at 1570°C [Fig. 3, arrow (*2*)]. We examined the variation of the relative intensities of the diffraction peaks of coexisting spinel and perovskite + periclase, as adopted in an earlier study to determine the phase boundary of the coesite-stishovite transformation in SiO_2 (*13*), by fixing the oil pressure, and only the temperature was changed. The pressure changed with changing temperature in a complex manner, depending on previous heating; in general, pressure dropped with decreasing temperature but recovered with increasing temperature.

The spinel-postspinel transformation occurred when the temperature was increased from 1600° to 1650°C, at about 21 GPa [Fig. 3, arrow (3)], and the reversal reaction proceeded when the temperature was decreased from 1800° to 1780°C at about 20.5 GPa [Fig. 3, arrow (4)]. Moreover, at the highest temperature of 1800°C, at pressures of 20.5 to

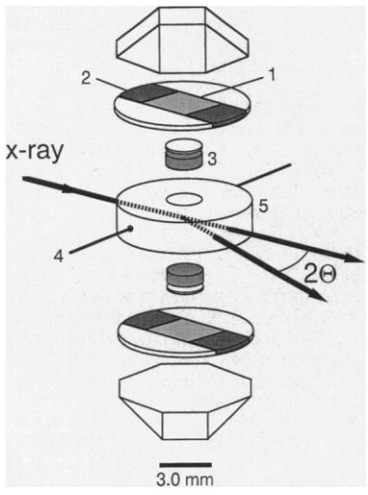

Fig. 1. Furnace and sample assembly used for the double-stage multianvil system with an anvil top of 3-mm edge length. 1, heater (TiC + diamond); 2, electrode (TiC); 3, sample (forsterite + Au); 4, thermocouple (W97Re3-W75Re25); and 5, pressure medium (MgO).

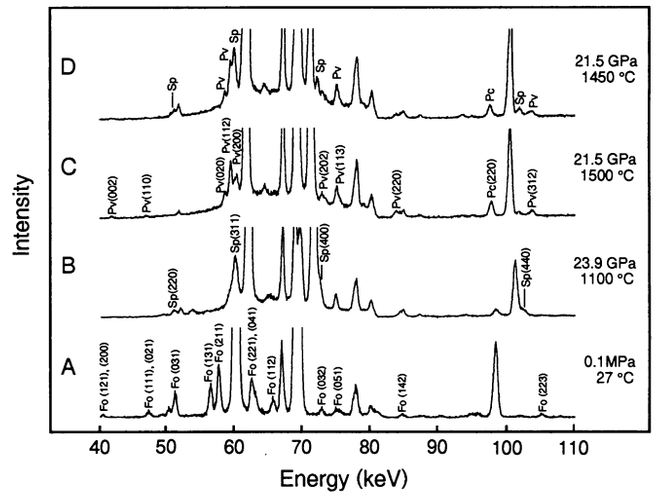

Fig. 2. The x-ray diffraction pattern of olivine starting material acquired at the ambient condition (**A**) in run S-010. The spinel phase metastably grew at about 24 GPa and at 1100°C (**B**), and a mixture of perovskite and periclase was observed at higher temperatures (**C**). When the temperature was slowly decreased, the partial conversion of this phase assembly into spinel was observed (**D**). The additional peaks are those of the diffraction and characteristic lines of Au, diffraction lines of magnesia pressure medium, and those of the W97Re3-W75Re25 thermocouple. Fo, Mg_2SiO_4 olivine; Pv, $MgSiO_3$ perovskite; Pc, MgO periclase.

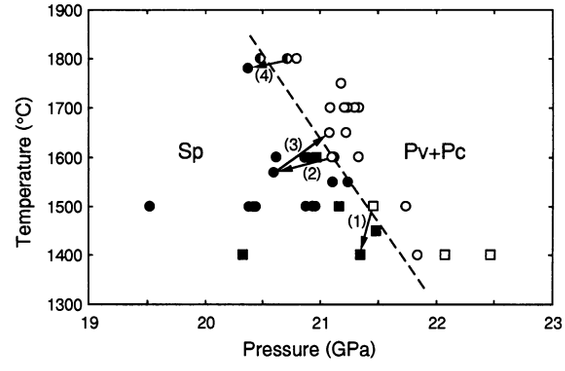

Fig. 3. Experimental conditions and results of two runs near the postspinel phase boundary in runs S-010 (squares) and S-012 (circles). Heating at each condition was typically for 20 min. In some cases, the phase transformation was apparent from the variations in the x-ray diffraction patterns when the temperature (and accordingly the pressure) was changed, which are indicated by the solid lines with arrows (see text). The postspinel phase boundary is located at 21.1 (±0.2) GPa, at 1600°C, a typical temperature estimation near the 660-km depth (*15*). Symbols denote the conditions in which the spinel/postspinel ratio increased (filled), decreased (open), or was without notable changes (half-filled).

20.7 GPa, no changes of the relative intensities were observed in spite of the long heating duration of about 60 min at such a high temperature. These observations indicate that the phase boundary is located close to 20.5 GPa at 1800°C, whereas it is near 21 GPa at 1600°C. We tried to constrain the phase boundary by changing the temperature, but it was difficult to judge the stability of phases because of possible grain coarsening and the slow reaction kinetics of the coexisting phases. The run was then quenched from 1450°C in the perovskite + periclase field.

An electron microprobe analysis was made on the quenched sample, and we confirmed that the product was composed of perovskite + periclase (Fig. 4). The grain size of perovskite was typically 3 to 5 μm, whereas the periclase grains were about 2 to 3 μm. The grain sizes are larger than those observed in quench experiments (*14*), presumably because S-012 was conducted near the phase boundary, and rapid nucleation of the coexisting phases could have been suppressed, allowing the growth of relatively large grains during heating for several hours at temperatures exceeding 1450°C.

The postspinel phase boundary determined by our experiments is fairly accurate, particularly at temperatures between 1400° and 1800°C (Fig. 3). The boundary has a negative Clapeyron slope (dT/dP) as indicated by the quench experiments and thermodynamic studies [for example (*3*, *4*)]. However, our study demonstrates that the boundary is located at about 21 GPa, at temperatures corresponding to the bottom of the mantle transition region [~1600°C (*15*)], which is about 2 GPa lower than that obtained in the earlier studies.

Although it has been suggested that the location of the 660-km seismic discontinuity can vary with depth by about ±30 km (*16*), the pressures corresponding to this discontinuity are mostly in a range between 22.5 and 24.5 GPa, which is higher than that of the postspinel phase boundary determined here. Thus, the *P-T* conditions of the experimental phase transformation and the inferred phase transformation at the 660-km discontinuity do not match.

If the temperatures of the mantle are lower than earlier estimates (*15*), then the mismatch may be resolved because the postspinel phase boundary shifts toward higher pressures because of its negative Clapeyron slope. In this case, however, the mantle temperature should be lower than about 1000°C at the 660-km discontinuity (Fig. 3). Such low temperatures are unrealistic in the mantle except for a limited region related to subducting slabs.

A likely explanation for the inconsistency is that the additional chemical components in the actual mantle composition may affect the postspinel transformation pressure. An important element bearing on this issue is ferrous iron (Fe^{2+}), which would replace about 10 atomic % of Mg in olivine in the mantle. However, the previous experimental study showed that an Fe substitution of this magnitude does not affect the pressure of the postspinel phase boundary (*3*). Nevertheless, such boundaries were not well determined by (*3*), because only a few experiments were used to constrain the phase diagram at such a composition range, in addition to the uncertainty of the pressure inherent in quench experiments. Other chemical species, such as Al_2O_3, CaO, Fe_2O_3, and H_2O, might also affect the postspinel transformation in complex chemical compositions representative of the mantle.

Pressure scales such as those adopted here might contain uncertainties, because no such volume-based scales have been vigorously tested under the *P-T* conditions of the present study. Although we confirmed the consistency of the pressure values using the equations of state for perovskite and periclase (*17*) with those derived from Au, it is possible that these currently available pressure scales are inaccurate. Development of techniques such as those based on simultaneous measurements of acoustic velocities and the *P-V-T* relations with synchrotron radiation (*18*) may help to obtain further accurate evaluation of the phase transformation pressures.

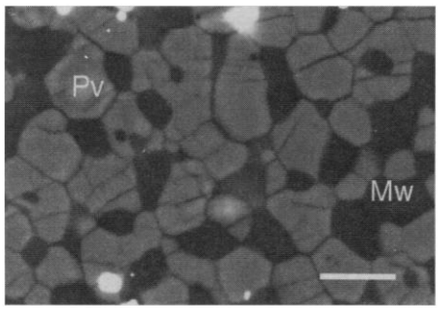

Fig. 4. A scanning electron micrograph of the run product obtained in S-012. The bright small patches are grains of Au used as the pressure marker. Bar, 5 μm.

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8. We used sintered magnesia as a pressure medium and pyrophyllite as the gasket material. Tungsten carbide cubes with truncated edge length (TEL) of 3.0 mm were used as the second-stage anvils. The heater was made of twin sheets of cemented TiC + diamond powders, and the temperature was measured by means of a W97Re3-W75Re25 thermocouple without correction of the effect of pressure on the thermoelectromotive force. The fluctuation of temperature was within ±0.5% throughout the present runs up to 1800°C. The temperature difference between the central and edge parts of the disk sample may be of the order of ±1 to 2% of the nominal temperature, as estimated by the textural observations of the run products and the melting behavior of Au in subsequent experiments. Further details of the cell design and experimental techniques will be given elsewhere (N. Nishiyama *et al.*, in preparation).
9. An equation of state proposed by O. L. Anderson, D. G. Isaak, and S. Yamamoto [*J. Appl. Phys.* **65**, 1534 (1989)] was used to calculate the pressure from the unit cell volume of Au. The consistency of this pressure scale with the established NaCl scale [D. L. Decker, *J. Appl. Phys.* **42**, 3239 (1971)] was confirmed by N. Funamori *et al.* [*J. Geophys. Res.* **101**, 8257 (1996)], which demonstrated that the differences of the pressures based on these two scales are within 0.2 to 0.4 GPa at temperatures 1000° to 1600°C and at pressures near 25 GPa.
10. These pressures at room temperature may be overestimated by 2 to 3 GPa because of the effect of deviatoric stress within the sample charge, which would approach zero upon heating above 600° to 800°C [D. J. Weidner *et al.*, *in High-Pressure Research: Application to Earth and Planetary Sciences*, Y. Syono and M. H. Manghnani, Eds. (Terrapub/American Geophysical Union, Tokyo/Washington, DC, 1992), pp. 13–17].
11. White x-rays from the synchrotron radiation available at a bending magnet beamline (BL04B1) at SPring-8 were directed to the sample near the hot junction of the thermocouple by horizontal (100 μm) and vertical (200 μm) slits, and the diffracted beam, collimated by a 100-μm horizontal slit, was detected with a Ge solid-state detector. We used a horizontally rotating goniometer, 2 θ being fixed at 5.0°, which was calibrated with the major four to five diffraction peaks of Au at the ambient pressure.
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17. We calculated the pressures at some temperatures on the basis of volume changes in $MgSiO_3$ perovskite and MgO periclase according to N. Funamori *et al.* [*J. Geophys. Res.* **101**, 8257 (1996)]. These results were generally consistent with those based on the Au scale, but yielded somewhat higher pressures. Nevertheless, the discrepancy was on the order of ~ 0.5 GPa and does not affect the present conclusion.
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19. We acknowledge N. Kubo for technical assistance and O. Shimomura for encouragement and useful comments. The x-ray experiments were carried out at SPring-8 (proposal No. 1997B0049-NOM-np).

12 December 1997; accepted 2 February 1998