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The phase boundary between wadsleyite and ringwoodite in Mg_2SiO_4 determined by in situ X-ray diffraction

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Abstract The phase boundary between wadsleyite and ringwoodite in Mg_2SiO_4 has been determined in situ using a multi-anvil apparatus and synchrotron X-rays radiation at SPring-8. In spite of the similar X-ray diffraction profiles of these high-pressure phases with closely related structures, we were able to identify the occurrence of the mutual phase transformations based on the change in the difference profile by utilizing a newly introduced press-oscillation system. The boundary was located at ~ 18.9 GPa and $1,400^\circ\text{C}$ when we used Shim's gold pressure scale (Shim et al. in *Earth Planet Sci Lett* 203:729–739, 2002), which was slightly (~ 0.8 GPa) lower than the pressure as determined from the quench experiments of Katsura and Ito (*J Geophys Res* 94:15663–15670, 1989). Although it was difficult to constrain the Clapeyron slope based solely on the present data due to the kinetic problem, the phase boundary [P (GPa) = $13.1 + 4.11 \times 10^{-3} \times T$ (K)] calculated by a combination of a P – T position well constrained by the present experiment and the calorimetric data of Akaogi et al. (*J Geophys Res* 94:15671–15685, 1989) reasonably explains all the present data within the experimental error. When we used Anderson's gold pressure scale (Anderson et al. in *J Appl Phys* 65:1535–1543, 1989), our

phase boundary was located in ~ 18.1 GPa and $1,400^\circ\text{C}$, and the extrapolation boundary was consistent with that of Kuroda et al. (*Phys Chem Miner* 27:523–532, 2000), which was determined at high temperature ($1,800$ – $2,000^\circ\text{C}$) using a calibration based on the same pressure scale. Our new phase boundary is marginally consistent with that of Suzuki et al. (*Geophys Res Lett* 27:803–806, 2000) based on in situ X-ray experiments at lower temperatures ($< 1,000^\circ\text{C}$) using Brown's and Decker's NaCl pressure scales.

Keywords Wadsleyite · Ringwoodite · Phase transformation · High pressure · In situ X-ray diffraction

Introduction

It is believed that the 520 km seismic discontinuity is attributable to the high-pressure phase transformation of olivine from wadsleyite to ringwoodite. Extensive high-pressure and high-temperature experimental studies of olivine–wadsleyite–ringwoodite transitions have been carried out in the system Mg_2SiO_4 – Fe_2SiO_4 . After the pioneering studies of Akimoto and Fujisawa (1968) and Ringwood and Major (1970), a more thorough study was conducted by Katsura and Ito (1989), who conducted quench experiments in which careful pressure calibrations were made using well-known phase transitions in specific reference materials. However, there remains significant uncertainty in the pressure measurement for these quench experiments. Akaogi et al. (1989) adopted an alternative approach, in which the transformation enthalpy from wadsleyite to ringwoodite was directly measured, and the phase boundary was calculated from these thermodynamic data. Owing to the difficulty of measuring the entropy of these phases, however, only one transition P – T point determined by Katsura and Ito (1989) was used to calculate the transition entropy. Thus, the pressure accuracy of this calculation depends to a large extent on the quality of the original data of Katsura and Ito (1989).

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Recently, Kuroda et al. (2000) determined the wadsleyite–ringwoodite phase boundary in quench experiments at 1,800–2,000°C, as determined based on a calibration using Anderson’s gold pressure scale as determined by in situ X-ray experiments. Suzuki et al. (2000) also determined this phase boundary by in situ X-ray measurement below 1,000°C, where the pressures were determined using Brown’s and Decker’s NaCl pressure scales. However, their boundaries are significantly different ($P=14.1+0.003\times T$ for Kuroda et al. (2000) and $P=10.3+0.007\times T$ for Suzuki et al. (2000), where P is the pressure (GPa) and T is the temperature (°C), because of the different Clapeyron slopes, their phase boundaries are as much as 2 GPa apart when extrapolated to 1,500°C. In spite of these differences, the phase boundary between 1,000 and 1,800°C, where a normal mantle geotherm should lie, has not been determined yet by in situ X-ray experiments, because of the high-temperature limitation of a NaCl pressure standard.

In the earlier runs of Kuroda et al. (2000) at Spring-8, significant crystal growth hindered accurate determination of the phase boundary by in situ X-ray measurement alone, at temperatures substantially higher than 1,000°C.

We conducted in situ X-ray diffraction experiments at Spring-8 to determine the high-pressure phase boundary between wadsleyite and ringwoodite in Mg_2SiO_4 at approximately 1,400°C, using Au as a pressure standard.

Experimental procedure

In situ X-ray experiments were conducted at high-pressure using an MA8-type high-pressure apparatus (SPEED-1500 and SPEED-MkII) installed at the bending magnet beamline (BL04B1) at the synchrotron facility in Spring-8, Japan (Utsumi et al. 1998; Katsura et al. 2004). Eight tungsten carbide cubes with 26 mm edges and truncated edge lengths of 3 mm were used as the second stage anvils. The incident white X-ray beam was reduced to 50 μm in the horizontal and 100 μm in the vertical direction using two slits with the beam directed to the sample through an anvil gap of ~ 1 mm under compression. The diffracted X-ray from the sample was collimated to 50 μm in the horizontal and 200 μm in the vertical direction, and collected by a Ge solid-state detector at a fixed diffraction angle (2θ) of 6°.

The furnace assembly in the double-stage system is shown in Fig. 1, and is similar to that used by Irifune et al. (1998). We used semi-sintered magnesia doped with 17 wt% CoO as a pressure medium, and pyrophyllite as gasket material. The heater was made of twin sheets of cemented TiC and diamond powder, oriented parallel to the incident and diffracted X-rays. Two BN sample capsules were filled with synthetic Mg_2SiO_4 and a mixture of Au and MgO powders (1:10 by weight), which serve as pressure references. In the present

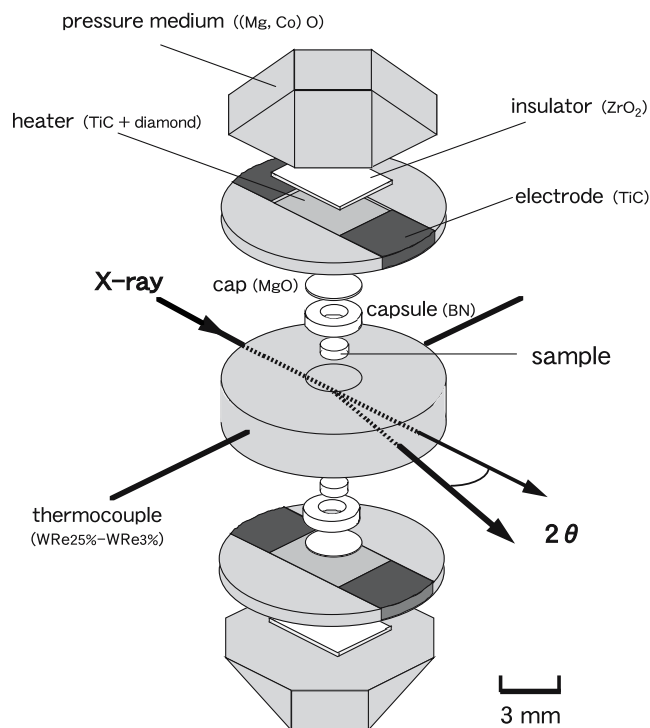


Fig. 1 Schematic illustration of the sample assembly used in the present experiment

experiments, we did not use NaCl as a pressure scale because it undergoes crystal growth and/or the melting at the P – T condition of interest. Au was also mixed with the Mg_2SiO_4 powder (1:5 in weight) except for run S387 in order to evaluate the pressure difference in two different mixtures. Temperature was measured with a $\text{W}_{75}\text{Re}_{25}$ – W_{97}Re_3 thermocouple of 0.05 mm in diameter. Temperature fluctuations were within $\pm 5^\circ\text{C}$ at each condition under which measurements were made. No pressure correction was made for the e.m.f. of the thermocouple.

Pressure was determined from the unit cell volume of Au using an equation of state (EOS) proposed by Shim et al. (2002) and Anderson et al. (1989). In some runs, we also used the MgO pressure scale proposed by Matsui et al. (2000) and Jamieson et al. (1982) for comparison. The precision of the pressure determination was normally within ± 0.2 GPa.

In the run of our first stage (S387), pressure was applied first to the target value, and then temperature was gradually increased until ringwoodite was formed, keeping the load constant. The X-ray diffraction pattern of the pressure marker and the sample were collected typically for 300 s at each P – T condition, and then the P – T conditions were changed by increasing the temperature. When a change was observed in the diffraction pattern, the charge was kept for longer time at those conditions in order to confirm the presence of a new phase. Weakening and/or disappearance of the diffraction peak were observed because of crystal growth. To confirm the identity of the phase present and/or the size

of the crystals, the charge was quenched to room temperature, and the recovered sample was examined by a micro-focused X-ray diffractometer and a scanning electron microscope (SEM) after polishing.

Figure 2 shows typical diffraction patterns of wadsleyite (β) and ringwoodite (γ) taken with a conventional X-ray diffractometer. Ringwoodite has a spinel structure, while wadsleyite has a modified spinel structure with a lower crystallographic symmetry. Thus, as seen in Fig. 2, all diffraction lines of ringwoodite appear in the diffraction profile of wadsleyite. This means that the transformation from ringwoodite to wadsleyite is easily detected, whereas the opposite is difficult. If we could not obtain the quasi-ideal diffraction of ringwoodite, it is impossible to judge the appearance of ringwoodite from the transformation of wadsleyite. To overcome this problem, we chose the direct increase of temperature to the desired P - T condition to prevent the crystal growth from the second stage experiments.

We also used oscillation system installed in SPEED-MkII to prevent the peak disappearance from the diffraction (Katsura et al. 2004) because of the crystal growth. This system was quite successful to get ideal diffraction pattern in spite of the limitation of the oscillation angle ($\sim 8^\circ$).

Results and discussion

First, we did three experiments (S387, S391 and S393) using SPEED-1500 without oscillation system. Next, we did three experiments (M097, M098 and M130) using SPEED-MkII with oscillation system. By these runs, we determined the phase boundary between wadsleyite and

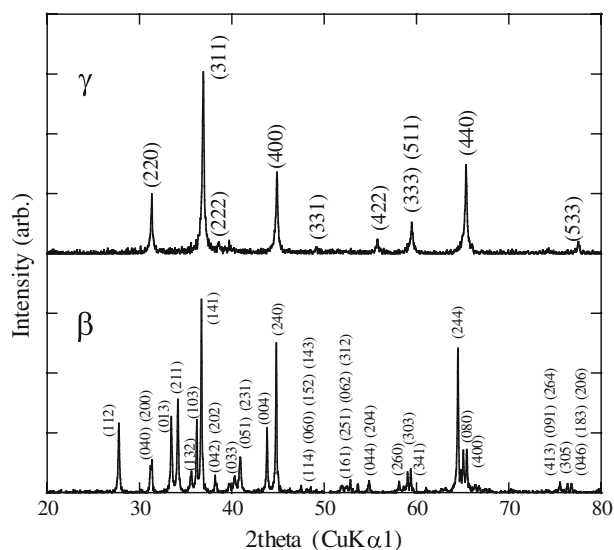


Fig. 2 Diffraction patterns of wadsleyite (β) and ringwoodite (γ) by conventional X-ray diffractometry. The wavelength of incident X-ray was 1.5405 Å, which was the characteristic X-ray of $\text{CuK}\alpha 1$. Wadsleyite and ringwoodite have modified-spinel and spinel structures, respectively, which imply that the split aspect of the diffraction profile from ringwoodite is recognized in wadsleyite

ringwoodite with forward and reverse reactions. The effect of the reaction kinetics is very significant to determine the phase boundary, so we had special attention to prevent such a problem by choosing the adequate P - T paths. The experimental conditions and the results of these runs are summarized in Table 1.

In run S387, the pressure was increased to 650 t ($P = \sim 22$ GPa) at room temperature, and then temperature was increased. Forsterite was used as a starting material.

At 700°C and ~ 20 GPa, peaks of ringwoodite were recognized from the starting forsterite, and a clear diffraction pattern for ringwoodite was obtained at 800°C and ~ 19 GPa.

We confirmed that ringwoodite was stable up to 1,300°C, and the diffraction line of wadsleyite (231) appeared at 1,400°C (Fig. 3). The charge was kept at 1,400°C for 27 min, and then at which time the peak of ringwoodite started to weaken, and the diffraction peaks almost disappeared. The charge was then heated to 1,500°C, but no new peaks were observed except for W (thermocouple) and cubic BN and MgO (surrounding materials). The charge was quenched at 1,500°C, and the sample was recovered.

In run S387, several ten microns of crystals were observed. Because of this phenomenon, the diffraction peaks of the sample disappeared during the in situ X-ray experiments. The micro-focused X-ray measurements conducted in the laboratory show that this phase is definitely wadsleyite. From this, we concluded that the transformation from ringwoodite to wadsleyite occurred at 18.4 GPa and 1,400°C in run S387.

In run S391, pressure was increased to 700 t, and then temperature was directly increased to 1,500°C (Fig. 4), and held constant for 60 min. Forsterite was used as a starting material, and Au was mixed in as a pressure marker. We confirmed that wadsleyite was the stable phase at these P - T conditions.

The same kind of experiment was conducted in run S393 at 750 t. At 1,500°C, ringwoodite was synthesized from forsterite at 19.7 GPa (Fig. 5). Temperature was kept constant at a load of 750 t for 60 min, but the pressure decreased slightly with time. As the pressure decreased, a wadsleyite peak appeared at 19.4 GPa after 22 min. And then, the diffraction peaks of wadsleyite were weakened due to crystal growth. The results of this run suggest that ringwoodite is stable at 19.7 GPa and 1,500°C and the transformation from ringwoodite to wadsleyite occurs at 19.4 GPa and 1,500°C.

To further confirm the phase boundary, especially the stability of ringwoodite from the transformation of wadsleyite, we conducted three additional experiments. In all experiments, we used wadsleyite as a starting material, and directly increased to the target P - T condition with rapid increase of temperature at constant load to prevent the crystal growth. In addition, we used oscillation system installed at SPEED-MkII to collect the quasi-ideal diffraction pattern of the phases (Figs. 6, 7, 8, 9).

Table 1 Experimental conditions and the results

Run No.	T (°C)	Time (min)	Au		MgO		S-A (GPa)	Phases	MgO a (Å)	Δa (Å)	V/V ₀	ΔV/V ₀	A [P (GPa)]	S [P(GPa)]	ΔP (GPa)	S-A (GPa)	J [P (GPa)]	M [P (GPa)]	M-J (GPa)
			a (Å)	Δa (Å)	V/V ₀	ΔV/V ₀													
M130022	1,300	10	4.0098	0.0003	0.9502	0.0002	18.13	18.89	0.04	0.76	β								
M130023	1,300	20	4.0093	0.0005	0.9499	0.0004	18.21	18.97	0.08	0.76	γ increase								
M130024	1,300	30	4.0092	0.0005	0.9498	0.0004	18.23	18.99	0.08	0.76	γ increase								
M130025	1,300	40	4.0096	0.0006	0.9501	0.0004	18.16	18.92	0.09	0.76	γ increase								
M130026	1,300	50	4.0094	0.0005	0.9499	0.0004	18.19	18.95	0.08	0.76	γ								
M130027	1,300	60	4.0093	0.0008	0.9499	0.0005	18.20	18.96	0.12	0.76	γ								
M130028	1,350		4.0111	0.0005	0.9512	0.0004	18.26	19.03	0.08	0.77	γ								
M130029	1,400		4.0128	0.0008	0.9524	0.0005	18.33	19.12	0.11	0.79	γ								
M130030	1,450	10	4.0171	0.0007	0.9554	0.0005	18.03	18.81	0.11	0.78	β appear								
M130031	1,450	20	4.0206	0.0005	0.9579	0.0004	17.52	18.27	0.07	0.75	β appear								
M130032	1,450	30	4.0207	0.0010	0.9580	0.0007	17.50	18.25	0.15	0.75	β appear								

A, S, J and M show the EOS of Anderson et al. (1989) and Shim et al. (2002) for Au, and those of Jamieson et al. (1982) and Matsui et al. (2000) for MgO, respectively. Δa, ΔV/V₀ and ΔP show the standard deviations of lattice parameter, relative unit cell volume and pressure, respectively. α, β and γ indicate olivine, wadsleyite and ringwoodite, respectively, and M shows marker which is the mixture of Au and MgO. Time means the passing time at a constant temperature and a constant load

In run M097, pressure was increased to 600 t, and temperature was increased to 1,300°C to release the deviatoric stress in the stability region of wadsleyite for ~20 min ($P=17.1$ GPa). Wadsleyite was used as a starting material, and Au was mixed in as a pressure marker. Then temperature was quenched and further compressed to 720 t. In this press load, temperature was directly increased to 1,300°C. At 18.5 GPa, the peaks of ringwoodite, especially (311) and (440) became stronger comparing with those of wadsleyite, though wadsleyite was still coexisted. At constant load, in general, pressure slightly decreased with increasing time at high temperature because of the cell weakening. To prevent this phenomenon, the press load was increased to 750 t (M097018-20), and then further increased to 800 t (M097021-23) to keep the generated pressure as constant. The peak of ringwoodite became strong with time at the pressure of 18.5 GPa, and we judged that the transformation from wadsleyite to ringwoodite occurred at 18.5 GPa and 1,300°C (Fig. 6).

In run M098, pressure was increased to 600 t, and temperature was increased to 1,400°C to release the deviatoric stress in the stability region of wadsleyite for ~10 min. Wadsleyite was used as a starting material, and Au was mixed in as a pressure marker. Then, temperature was quenched and further compressed to 850 t. In this press load, temperature was directly increased to 1,400°C. The clear diffraction pattern of ringwoodite was obtained at 19.2 GPa and 1,400°C by the transformation from wadsleyite (Fig. 7).

In run M130, pressure was increased to 600 t, and temperature was increased to 1,300°C to release the deviatoric stress in the stability region of wadsleyite for ~80 min. Wadsleyite was used as a starting material, and Au was mixed in as a pressure marker. Then, temperature was quenched and further compressed to 800 t. In this press load, temperature was directly increased to 1,300°C ($P=17.6$ GPa). The transformation to ringwoodite did not occur in this condition, so the charge was quenched to room temperature and further compressed to 900 t. In this press load, temperature was directly increased to 1,300°C again ($P=18.6-18.8$ GPa), but the transformation did not occur in this condition during 75 min heating. So the charge was quenched again to room temperature and further compressed to 930 t. In this press load, temperature was directly increased to 1,300°C again ($P=18.9-19.0$ GPa). The transformation to ringwoodite was observed in this condition during 70 min heating (Fig. 8). Then temperature was increased gradually to 1,400°C, and then 1,450°C, and the reverse transformation to wadsleyite was observed at 18.8 GPa and 1,450°C (Fig. 9).

Thus we could constrain four forward and four reverse transformation $P-T$ conditions on the phase boundary between wadsleyite and ringwoodite in the temperature range of 1,300–1,500°C.

We calculated the phase boundary between wadsleyite and ringwoodite using the thermochemical data listed in Tables 3 and 4 in Akaogi et al. (1989). A single

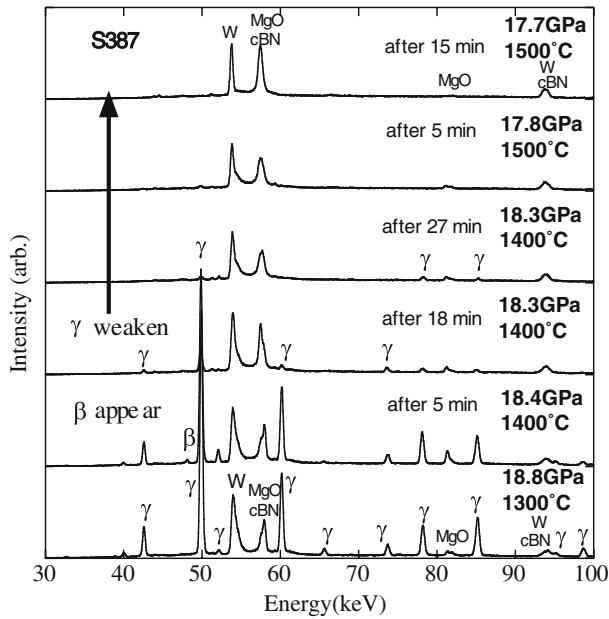


Fig. 3 The X-ray diffraction pattern of the sample in run S387. β , wadsleyite; γ , ringwoodite; cBN, cubic BN; W, tungsten (thermocouple). The diffraction patterns were collected in the conditions from bottom to top direction. The peaks of wadsleyite appeared at 18.4 GPa, 1,400°C and almost peaks were weakened above 1,400°C. Time shows the passing time at a constant temperature and constant load

P , T point (18.9 GPa and 1,400°C) from our study was used to calculate the transformation entropy; the obtained value (-7.2 ± 1.3 J/mol K) is slightly different from that calculated by Akaogi et al. (1989)

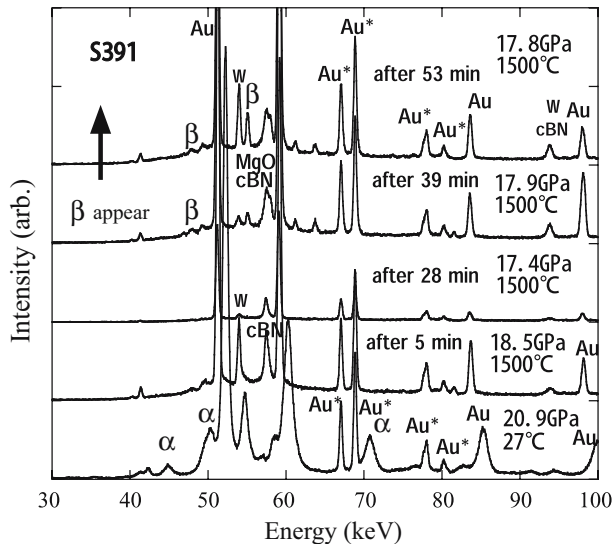


Fig. 4 The X-ray diffraction pattern of the sample in run S391. The sample was mixed with Au powder and the diffraction patterns of Au were observed. Au* shows characteristic line of Au, and α shows olivine. The temperature was increased rapidly to 1,500°C and kept for ~ 60 min. The peaks of wadsleyite appeared at 17.9 GPa, 1,500°C. Time shows the passing time at a constant temperature and constant load

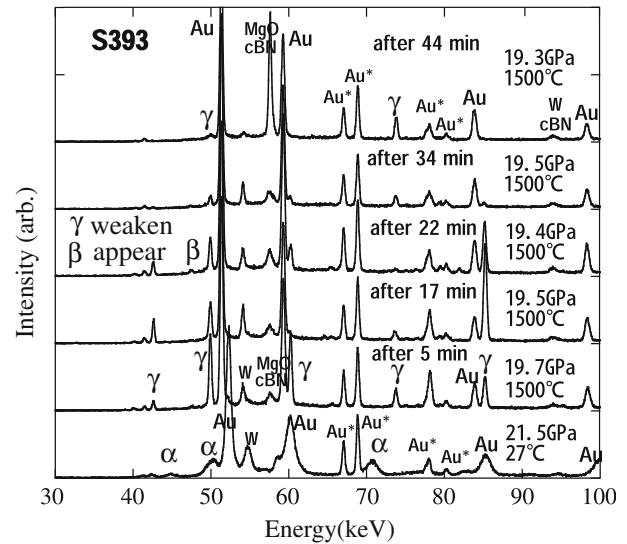


Fig. 5 The X-ray diffraction pattern of the sample in run S393. The sample was mixed with Au powder and the diffraction patterns of Au were observed. Au* shows characteristic line of Au. The temperature was increased rapidly to 1,500°C and kept for ~ 60 min. The peaks of wadsleyite appeared at 19.4 GPa, 1,500°C and the almost peaks of the sample were weakened with time. Time shows the passing time at a constant temperature and constant load

(-7.5 ± 1.4 J/mol K), because they used the different P , T point by Katsura and Ito (1989) (18.5 GPa and 1,200°C). The present phase boundary is given by the following equation: $P = 13.1 + (4.11 \times 10^{-3}) \times T$, where P is

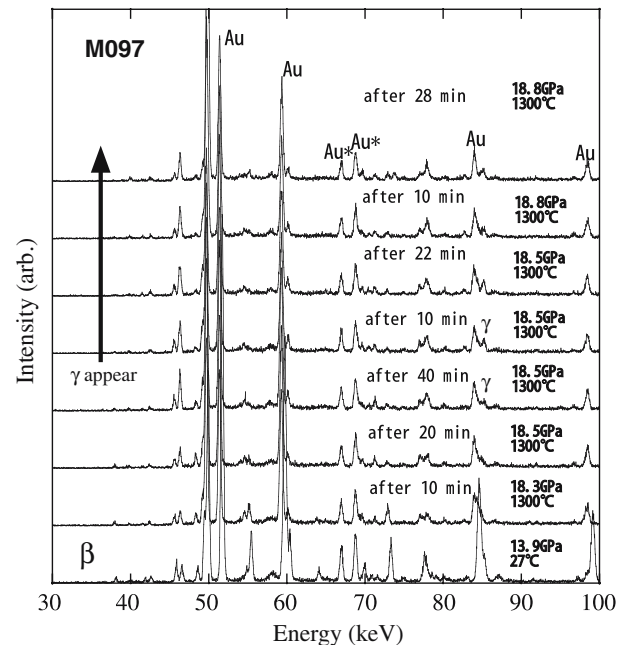


Fig. 6 The X-ray diffraction pattern of the sample in run M097. The sample was mixed with Au powder and the diffraction patterns of Au were observed. Au* shows characteristic line of Au. The temperature was increased rapidly to 1,300°C. The peaks of ringwoodite appeared at 18.5 GPa, 1,300°C. Time shows the passing time at a constant temperature and constant load

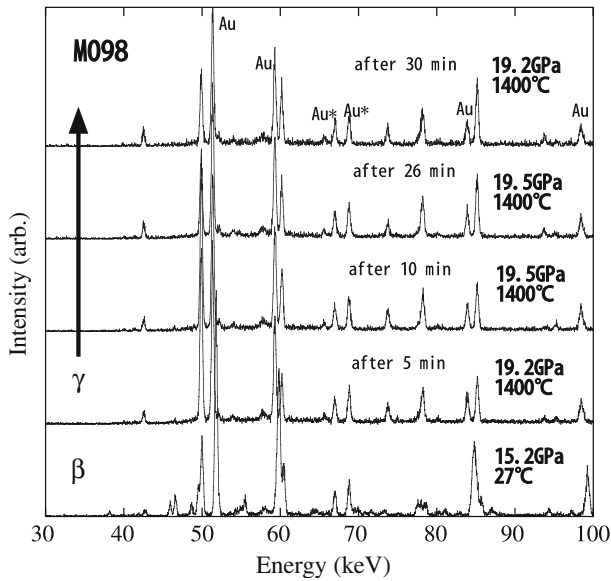


Fig. 7 The X-ray diffraction pattern of the sample in run M098. The sample was mixed with Au powder and the diffraction patterns of Au were observed. Au* shows characteristic line of Au. The temperature was increased rapidly to 1,400°C. The peaks of ringwoodite appeared at 19.2 GPa, 1,400°C. Time shows the passing time at a constant temperature and constant load

the pressure (GPa) and T is the temperature (°C). This equation accounts for all of the data in the present study within the error; these results are plotted in Fig. 10 in terms of pressure and temperature, along with the calculated phase boundary.

Figure 11 shows a comparison of our results with previous phase boundaries between wadsleyite and

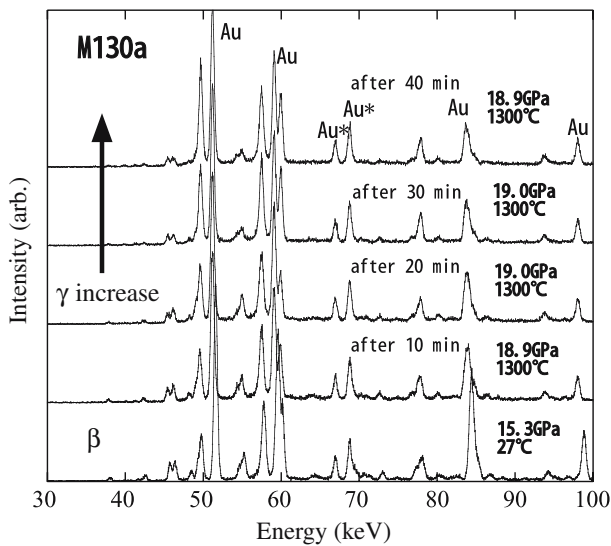


Fig. 8 The X-ray diffraction pattern of the sample in run M130a. The sample was mixed with Au powder and the diffraction patterns of Au were observed. Au* shows characteristic line of Au. The temperature was increased rapidly to 1,300°C. The peaks of ringwoodite appeared at 19.0 GPa, 1,300°C. Time shows the passing time at a constant temperature and constant load

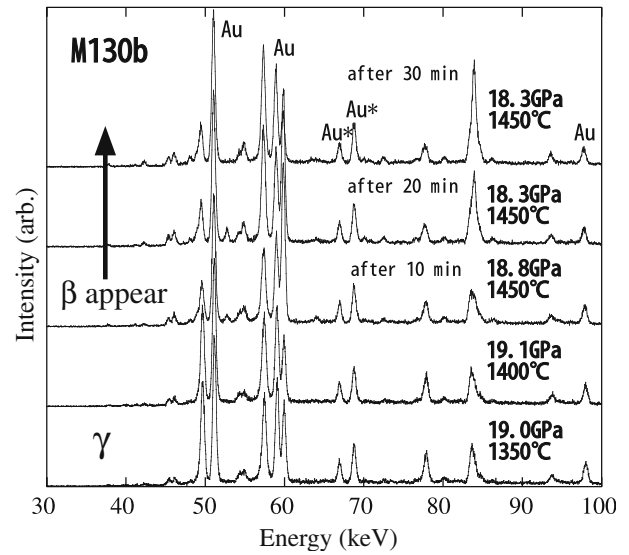


Fig. 9 The X-ray diffraction pattern of the sample in run M130b. The temperature was increased from 1,350°C to 1,400°C, and 1,450°C. The peaks of wadsleyite appeared at 18.8 GPa, 1,450°C. Time shows the passing time at a constant temperature and constant load

ringwoodite reported by other workers (Katsura and Ito, 1989; Akaogi et al. 1989; Kuroda et al. 2000; Suzuki et al. 2000). The present transformation is located at ~ 18.5 and ~ 19.3 GPa, at temperatures of 1,300 and 1,500°C, respectively; these pressures are ~ 0.5 – 0.8 GPa lower than those reported by Katsura and Ito (1989) and

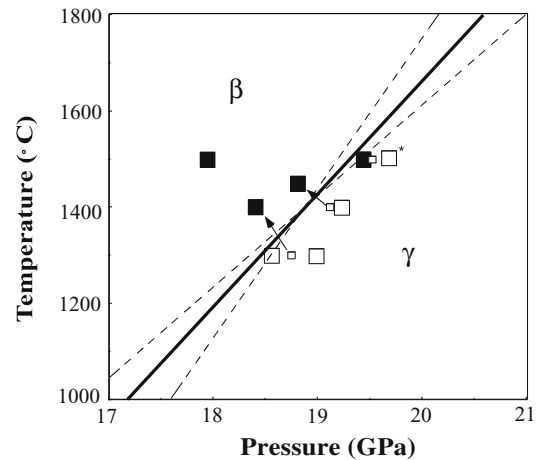


Fig. 10 Critical transformation points from ringwoodite to wadsleyite, and from wadsleyite to ringwoodite constrained by the present six in situ runs. Pressure was calculated by Shim's equation state of gold. Large open and closed symbols show the transformation points from wadsleyite to ringwoodite and from ringwoodite to wadsleyite, respectively. Small open symbols show the ringwoodite stable points just before the transformation to wadsleyite. The phase boundary was calculated by the reported transformation enthalpy from Akaogi et al. (1989) as a fixed point of 18.9 GPa and 1,400°C. The solid line shows the calculated phase boundary, while the dashed line shows the uncertainty of the slope of the calculated boundary due to the errors of the thermochemical data

Akaogi et al. (1989). Katsura and Ito (1989) conducted quench experiment using a conventional pressure calibration. Akaogi et al. (1989) used one P - T point from Katsura and Ito (1989) to calculate the phase boundary. In our study, we conducted in situ X-ray analyses and adopted the EOS of Au from Shim et al. (2002) to calculate the absolute pressure. The differences in the position of the phase boundary arise from the method by which pressure was determined in each study. We argue that the results of the in situ X-ray experiment are more reliable than quench experiments, in terms of internal consistency.

When we use the Au pressure scale proposed by Anderson et al. (1989), our phase boundary is consistent with the extrapolation of Kuroda et al. (2000), who determined the phase boundary in quench experiments based on the same pressure calibration in their in situ X-ray experiments.

Recently, Suzuki et al. (2000) determined the phase boundary between wadsleyite and ringwoodite below 1,000°C by in situ X-ray experiments, based on the NaCl pressure scale proposed by Decker (1971) and Brown (1999). Their Clapeyron slope is slightly different from our slope, but consistent with ours within experimental uncertainty.

We used the Au pressure scale of Shim et al. (2002) to calculate the generated pressure. On the other hand, the scale of Anderson et al. (1989) is also used as a pressure standard for in situ X-ray experiments. Shim's EOS

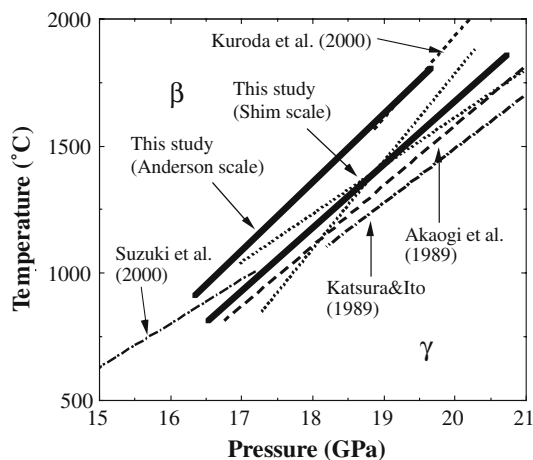


Fig. 11 The comparison with the other pressure scale of gold (Anderson et al. 1989) and the other results reported previously (Katsura and Ito 1989; Akaogi et al. 1989; Kuroda et al. 2000; Suzuki et al. 2000). The Anderson's scale yields ~ 0.7 – 0.8 GPa lower pressure than Shim's scale in the present P - T range. Even if we use Shim's scale, the present boundary is ~ 0.8 GPa lower than that of Katsura and Ito (1989) determined by quench experiment. The present phase boundary calculated by Anderson's EOS is consistent with Kuroda et al. (2000), and marginally consistent with low temperature boundary of Suzuki et al. (2000). The *dashed line* of this study (Shim scale) shows the uncertainty of the slope of the calculated boundary due to the errors of the thermochemical data

yields ~ 0.7 – 0.8 GPa higher pressure than Anderson's EOS in the pressure of 17–19 GPa at around 1,500°C.

We also checked the difference between the pressures calculated using Au in the mixture of Au + MgO and Au + Mg₂SiO₄, in order to test the effects of the surrounding materials on the pressure calibration. The pressure difference was within 0.3 GPa, and generally consistent with each other. (In run S391, the significant pressure decrease was observed in the first stage of heating at 1,500°C; this indicates cell weakening.)

MgO is also often used as a pressure marker, and we checked the pressure difference between MgO and Au in some runs. Some pressure scales have been proposed for MgO, and we chose the EOS of Jamieson et al. (1982) and Matsui et al. (2000) for calculating the pressure. Matsui's EOS yields ~ 1.0 GPa higher pressure than Jamieson's EOS in the pressure of 17–19 GPa at around 1,500°C.

We compared the pressure calculated with Matsui's MgO scale and Anderson's Au scale. In our new data set, the pressure difference due to the different scales is ~ 0.5 GPa at 17–19 GPa and 1,300–1,400°C, though some data show the difference of up to ~ 1.0 GPa. Matsui and Nishiyama (2002) reported the corresponding difference is 1.4 ± 0.3 GPa at slightly higher pressures of 20–22 GPa, at 1,600°C. Considering the different P/T conditions of these studies, we conclude that these data sets are consistent each other. Although some significant scatterings in pressure were observed in our and Matsui and Nishiyama (2002)'s data set, this may be due to the deviatoric stresses retained at even such a high temperature in the mixture of MgO and Au.

Shim's Au EOS shows the almost same value or even higher than Matsui's MgO EOS. Nevertheless, the present phase boundary based on Shim's EOS is lower pressure than those of Katsura and Ito (1989).

Recently, Tsuchiya (2003) also presented the EOS of Au from the first-principle prediction, and found that the EOS provides a 1.3 GPa higher pressure than Anderson's scale at 23 GPa and 1,800 K. As Shim's scale provides 1.0 GPa higher pressure than Anderson's scale at the condition, Tsuchiya's scale provides 0.3 GPa higher pressure than Shim's scale. Thus, when we use Tsuchiya's scale, the discrepancy is slightly reduced, but still exists.

We conclude that the best estimation of the phase boundary between wadsleyite and ringwoodite in Mg₂SiO₄ is obtained by in situ X-ray diffraction measurements. These results are useful for the determination of the thermal structure of the mantle in the vicinity of the 520 km seismic discontinuity. Of course, the effect of iron on the phase transformation between wadsleyite and ringwoodite must also be considered. According to Katsura and Ito (1989) and Akaogi et al. (1989), the phase boundary in mantle olivine composition (Mg_{0.9}Fe_{0.1})₂SiO₄ is ~ 2.0 – 2.5 GPa smaller than that in the pure Mg₂SiO₄ system. When these differences are taken into account, the pressure of the phase transformation in mantle olivine composition is ~ 17.0 –

17.5 GPa, which is slightly lower than those corresponding to the 520 km seismic discontinuity (equivalent to ~ 18.0 GPa). This discrepancy is the same as reported by Shim et al. (2002), who studied the post-spinel boundary which should be related to the 660 km seismic discontinuity.

Since the study of Irifune et al. (1998) who used Anderson's Au EOS to determine post-spinel boundary, there are a lot of controversies about the pressure scale used in the in situ X-ray experiment. As shown in the present study, we regret to say that there is no reliable absolute pressure scale in the present stage. High-pressure X-ray experiments, however, give us the internally consistent data set, especially the relative volume change under high pressure and temperature, so we listed the relative volume data in Table 1. Further studies are needed to introduce the reliable pressure scale. In addition, the thermocouple e.m.f. dependence on pressure may also be important to clarify this problem.

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