# Water partitioning in the Earth's mantle

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**Abstract** We have conducted $H_2O$ partitioning experiments between wadsleyite and ringwoodite and between ringwoodite and perovskite at 1673K and 1873K, respectively. These experiments were performed in order to constrain the relative distribution of $H_2O$ in the upper mantle, the mantle transition zone, and the lower mantle. We successfully synthesized coexisting mineral assemblages of wadsleyite-ringwoodite and ringwoodite-perovskite that were large enough to measure the $H_2O$ contents by secondary ion mass spectrometry (SIMS). Combining our previous $H_2O$ partitioning data (Chen et al., 2002) with the present results, the determined water partitioning between olivine, wadsleyite, ringwoodite, and perovskite under $H_2O$-rich fluid saturated conditions are 6: 30: 15 : 1, respectively. Because the maximum $H_2O$ storage capacity in wadsleyite is ~3.3 wt% (e.g. Inoue et al, 1995), the possible maximum $H_2O$ storage capacity in the olivine high pressure polymorphs are as follows: ~0.7 wt% in olivine (upper mantle just above 410 km depth), ~3.3 wt% in wadsleyite (410-520 km depth), ~1.7 wt% in ringwoodite (520-660 km depth), and ~0.1 wt% in perovskite (lower mantle). If we assume ~0.2 wt% of the $H_2O$ content in wadsleyite in the mantle transition zone estimated by recent electrical conductivity measurements (e.g. Dai and Karato, 2009), the estimated $H_2O$ contents throughout the mantle are as follows; ~0.04 wt% in olivine (upper mantle just above 410 km depth), ~0.2 wt% in wadsleyite (410-520 km depth), ~0.1 wt% in ringwoodite (520-660 km depth) and ~0.007 wt% in perovskite (lower mantle). Thus, the mantle transition zone should contain a large water reservoir in the Earth's mantle compared to the upper mantle and the lower mantle.

Key words: mantle, olivine, wadsleyite, ringwoodite, perovskite, hydrous wadsleyite, hydrous ringwoodite, high pressure phase transformation, partitioning of $H_2O$

## 1. Introduction

Water, the most abundant volatile component on the Earth's surface, has been supplied to the Earth's mantle by subducting slabs from the lithosphere (e.g. Irifune et al.,1998; Ohtani et al., 2004). Because water influences the physical properties and melting temperature of minerals, it is important to constrain the potential amount of water in nominally anhydrous phases at various depths in the Earth's mantle.

Olivine (α-phase) and the high pressure polymorphs of olivine are the most abundant minerals in the upper mantle, and the high-pressure polymorphs of olivine, wadsleyite (β-phase), and ringwoodite (γ-phase), can contain up to 2-3 wt% of $H_2O$ in their crystal structures (e.g. Inoue et al., 1995, 1998; Kohlstedt et al., 1996). However, the partitioning data of $H_2O$ between these minerals are few except for the olivine-wadsleyite transformation (Chen et al., 2002) and ringwoodite-perovskite transformation (Bolfan-Casanova et al., 2003). We have determined the partitioning of $H_2O$ between wadsleyite and ringwoodite and between ringwoodite and perovskite at 1673K and 1873K, respectively. These temperatures are close to typical mantle temperature proposed by Brown and Shankland (1981) and Katsura et al. (2009) at the 520 km and 660 km seismic discontinuity. We have also ascertained the relative distribution of $H_2O$ among the upper mantle, the mantle transition zone, and the lower mantle.

## 2. Experimental

High-pressure experiments were conducted in an MA-8 type (Kawai-type) high-pressure apparatus at Ehime University. The truncation edge lengths (TEL) of the cubic anvils were 3.5 and 2.5 mm for the experiments on wadsleyite-ringwoodite and ringwoodite-perovskite, respectively. We used semi-sintered magnesia that was doped with 17 wt % CoO and $LaCrO_3$ as the pressure medium, and $ZrO_2$ was used as the thermal insulator. We adopted a cylindrical platinum (Pt) or rhenium (Re) heater with a wall thickness of ~30 μm. The typical cell assembly used with TEL of 3.5 mm is shown in Fig. 1.

The starting materials were a mixture of $Mg(OH)_2$, $Fe_2SiO_4$ and $SiO_2$ reagent with the

chemical composition of $(Mg_{0.8}Fe_{0.2})_2SiO_4$ plus 15.8 wt% $H_2O$ (Table 1). Thus, $H_2O$ was introduced by $Mg(OH)_2$, and ferrous iron was introduced by $Fe_2SiO_4$ because wustite ($Fe_{1-X}O$) is non-stoichiometric. The reason we selected such large water content was to enhance the crystal growth and to make it possible to measure the $H_2O$ content precisely by secondary ion mass spectroscopy (SIMS). In addition, the reason we selected the olivine composition of $(Mg_{0.8}Fe_{0.2})_2SiO_4$ was to enhance the coexisting region of wadsleyite-ringwoodite and ringwoodite-perovskite in order to obtain the sample.

A corresponding anhydrous starting material was also prepared. The appropriate mechanical mixture of $Mg_2SiO_4$ and $Fe_2SiO_4$ powders was used for the composition of $(Mg_{0.8}Fe_{0.2})_2SiO_4$. Both anhydrous and hydrous samples were enclosed in a welded $Au_{75\%}Pd_{25\%}$ alloy capsule separately before loading into a high pressure cell in order to avoid the loss of both water and iron. Platinum is often used as capsule material, but it absorbs iron significantly. Therefore, we used Au75%Pd25% to make the loss of Fe less, which is superior to Pt in an iron bearing system, as the capsule material.

Temperature was measured with a $W_{97}Re_3$-$W_{75}Re_{25}$ thermocouple junction placed in the center of the furnace assembly. The fluctuation of temperature throughout the run was kept within ±5 ℃ in each condition, but no pressure correction was made for the emf of the thermocouple.

Careful pressure calibration was done on the basis of the present anhydrous experiments of the wadsleyite-ringwoodite phase transition based on the thermochemical phase diagram (Akaogi et al., 1989) at 1673K, and the postspinel phase transition (Ito and Takahashi, 1989) at 1873K. Therefore, the pressure conditions for the coexisting run products wadsleyite-ringwoodite and ringwoodite-perovskite were determined by fitting our anhydrous compositional data on the loop by Akaogi et al.(1989) and Ito and Takahashi (1989). In this case, the relative pressure precision in the runs with the coexisting wadsleyite-ringwoodite and coexisting ringwoodite-perovskite under anhydrous conditions is estimated to be about 0.05 GPa, and about 0.2 GPa in runs without co-existing phases.

In high-pressure and high-temperature experiments, pressure was applied first to the target ram loads, then the temperature was kept constant for 20-120 minutes before quenching by turning off power to the furnace, and then the run was quenched by

turning off the electric power. The recovered charges were polished for phase identification and chemical analysis.

The phases were identified by a micro-focused X-ray diffractometer and by micro-Raman spectroscopy. The chemical compositions were determined by EPMA and the water content of the minerals was measured by SIMS at Hokkaido University.

The SIMS instrument used in the present study was the Cameca IMS-3F ion mass microanalyzer. The polished samples were coated with a gold film 300Å in thickness for SIMS analysis. A primary beam operated at ~10 nA, 12.5 kV $^{16}O^-$ was focused to form an ~30 μm spot on the sample, and the secondary $^{1}H^+$ and $^{30}Si^+$ ions were collected from the center region (10 μm in diameter) of the sputtered area using a mechanical aperture to minimize artifacts arising from hydrogen adsorption on the polished sample surface. The $H_2O$ content of samples was calibrated from relative intensities of $^{1}H^+/^{30}Si^+$ using an empirical linear relationship (Yurimoto et al., 1989). We used natural amphibole crystal with a water content of 1.66 wt % for a standard, which was determined by a hydrogen gas manometry method with the accuracy of ±0.1 wt% (Miyagi and Yurimoto, 1995). In addition, San Carlos olivine was used for the background H intensities, because the H concentration is considerably small (10-60 ppm: Kurosawa et al. 1997), compared with the present H concentration in our samples.

We obtained a depth profile of the intensity of $^{1}H^+$ and $^{30}Si^+$ with time. The steady-state hydrogen emission achieved depends on the H concentration, but usually it is achieved after 30-60 minute bombardments of the primary ions with $H_2O$ concentration of ~1 wt%. The uncertainty of the $H_2O$ content in the present analysis is ~ ±10%, which mainly comes from the scattering of the measured $^{1}H^+/^{30}Si^+$ value for several standard measurements, probably because of the slightly chemical heterogeneity of the present natural amphibole standard. More details for the SIMS measurement are described in Miyagi and Yurimoto (1995), and the water content and the chemical composition of the present amphibole standard was shown in Table 1 (ICH) of Miyagi et al. (1998).

## 3. Results and discussion

The experimental conditions and results are summarized in Tables 2 and 3. The experiments were conducted at conditions of 14.6-17.0 GPa and 1673K for the wadsleyite-ringwoodite experiment and ~23 GPa and 1873K for the

ringwoodite-perovskite experiments. The heating durations were 20-120 minutes.

All experiments were performed under $H_2O$-rich fluid (melt) saturated conditions where solid phases coexisted with a hydrous melt, as evidenced by fibrous crystals and spinifex texture in the quench product. These results show the formation of liquid under all conditions.

Note that at the present experimental conditions in the silicate-$H_2O$ system, $H_2O$-bearing silicate melt (liquid) and $H_2O$-rich aqueous fluid cannot be distinguished from each other because of the existence of the second critical end point (e.g. Mibe et al., 2007). So the terminology of melt (liquid) and fluid in this paper has the same meaning.

### 3-1. The effect of water on the phase boundary between wadsleyite and ringwoodite

We observed the coexistence of wadsleyite and ringwoodite at pressures of 15.6 to 16.5 GPa under anhydrous conditions, whereas the coexistence of both wadsleyite and ringwoodite were not observed below 16.4 GPa under hydrous conditions (Table 2). This shows that the phase boundary between wadsleyite and ringwoodite moves to higher pressure under water-bearing conditions.

Table 4 shows the Fe/(Mg+Fe) in wadsleyite and ringwoodite and the corresponding partition coefficient at each pressure. We define the partition coefficient, Kd, as $(Fe/Mg)_{\gamma}/(Fe/Mg)_{\beta}$. The Kds were ~1.6-1.7 in both the anhydrous and hydrous systems, which are consistent with our previous report (Inoue et al, 2010).

Figures 2(a) and 2(b) show the high pressure phase diagrams of wadsleyite and ringwoodite in the $Mg_2SiO_4$-$Fe_2SiO_4$ system under anhydrous and hydrous conditions, respectively, by using the present Fe/(Mg+Fe) data for wadsleyite and ringwoodite.

At 15.6 GPa (Run E1766), the coexistence of wadsleyite and ringwoodite starts to appear in the anhydrous system, but ringwoodite does not appear in the hydrous system. This trend for the anhydrous and hydrous systems continues up to 16.5 GPa (Run E1794), and the coexistence of wadsleyite and ringwoodite appears at 16.5 GPa (Run E1760, E1751) in the hydrous system. In run E1788 (P=~17 GPa), only ringwoodite was observed under anhydrous conditions, but the coexistence of wadsleyite and ringwoodite was still observed under hydrous conditions.

This result indicates that the loop of the wadsleyite and ringwoodite boundary shifts towards higher pressure or higher iron content, and the pressure width of the loop decreased with the effect of $H_2O$. The present observation is consistent with our previous result of 1 wt% $H_2O$ (Inoue et al., 2010).

We have already determined that the phase boundary between olivine and wadsleyite shifts to lower pressures under water bearing conditions (Chen et al., 2002; Inoue et al., 2009). Combining the present results with our previous data, it is clear that the stability region of wadsleyite expands and the pressure width of the divariant loop decreases for both of the phase boundaries between olivine and wadsleyite, and between wadsleyite and ringwoodite.

In the present study, the experiments were performed under $H_2O$-rich fluid saturated conditions, so note that the width of the loop can only be applied to $H_2O$-rich fluid saturated conditions, and the width of the loop should be narrower than those in $H_2O$-rich fluid undersaturated conditions when considering the phase diagram of the pure-Mg system (Frost and Dolejs, 2007). However, the important point is that the amounts of Mg and Fe in the coexisting phases are different between anhydrous and hydrous conditions (Inoue et al.2010). The present results reflect the system with Mg-Fe partitioning under $H_2O$-rich fluid saturated condition.

For the hydrous melting phase relation, clinoenstatite was observed in the liquidus phase below ~17 GPa, and then changed to stishovite. These results indicate that MgO-rich (ultrabasic) liquid was formed under hydrous melting conditions, which are consistent with our previous results (Inoue at al., 1994; Yamada et al., 2004).

### 3-2. The effect of water on postspinel phase boundary

The coexisting region of ringwoodite and perovskite was quite narrow in both the anhydrous and hydrous systems, so it was difficult to determine the exact loop in this boundary. However, we could observe the coexistence of ringwoodite and perovskite at pressures of 23.0-23.2 GPa (runs E1784, E1730 and E1695).

At 23.0 GPa (E1784), the Fe/(Mg+Fe) ratios in ringwoodite, perovskite, and magnesiowustite were 0.199, 0.086 and 0.342, respectively, whereas in the hydrous system, the Fe/(Mg+Fe) ratios in ringwoodite and perovskite were 0.159 and 0.056, respectively. We could not observe magnesiowustite in the most hydrous run, because the composition of the hydrous liquid became MgO rich with increasing pressure, as we

have already reported (Inoue, 1994; Yamada et al., 2004), and magnesiowustite tends to dissolve in the liquid. The reason why the Fe/(Mg+Fe) ratios of ringwoodite and perovskite in the hydrous system is much lower than those in anhydrous conditions is the existence of the hydrous liquid. The hydrous liquid prefers iron compared to crystalline phases. Nevertheless, the partition coefficients, Kd = $(Fe/Mg)_{Pv}/(Fe/Mg)_{\gamma}$, were almost the same (~0.3~0.4) in both anhydrous and hydrous systems.

We have already reported the effect of water on the spinel-postspinel transformation in $Mg_2SiO_4$, and reported that the boundary moves to high pressures by ~0.2 GPa under water bearing conditions, compared with anhydrous conditions (Higo et al., 2001). In the present experiment, we could not observe the phenomena clearly because of the fluctuation of the generated pressure in each cell assembly. In the hydrous system this was also caused by the complicated phase assembly in each run. Nevertheless, the main purpose of the present experiment was to obtain the coexisting sample of ringwoodite and perovskite to determine the $H_2O$ content and the partitioning effect. We succeeded in this purpose, which will be further described later.

### 3-3. The $H_2O$ content and partitioning in wadsleyite, ringwoodite and prerovskite

We succeeded in synthesizing large (~50μm) crystals of coexisting wadsleyite and ringwoodite, and of ringwoodite and perovskite. Figures 3 and 4 show the back scattered electron images of the coexisting run products of wadsleyite and ringwoodite (E1751, E1760), and of ringwoodite and perovskite (E1748 and E1730), respectively. In all run products, hydrous liquids coexisted with the minerals. In addition, clinoenstatite existed in the liquidus phase at ~16.5 GPa and 1673K under hydrous melting conditions.

Table 6 shows the $H_2O$ contents in wadsleyite and ringwoodite at ~16.5 GPa and 1673K, and the corresponding partition coefficient. The $H_2O$ contents in wadsleyite and ringwoodite at ~16.5 GPa and 1673K were 1.8-2.3 wt% and 1-1.25 wt%, respectively. In E1788, the $H_2O$ content was higher than that in the other runs, because the temperature was estimated by the power supply and the generated temperature may have been lower than 1673K. For this reason, the amount of hydrous melt was small and the $H_2O$ contents in the crystals became higher in E1788. In spite of this difference, the partition coefficient between wadsleyite and ringwoodite ($Kd=(H_2O)_{\beta}/(H_2O)_{\gamma}$) was ~2;

this result shows that wadsleyite favors $H_2O$ twice as much when compared to ringwoodite.

Table 7 shows the $H_2O$ content in ringwoodite and perovskite at ~23 GPa and 1873K, and the partition coefficient. The $H_2O$ content in ringwoodite and perovskite at ~23 GPa and 1873K were 0.6-0.8 wt% and less than 0.1 wt%, respectively. Because the $H_2O$ content in perovskite was quite small, the resulting calculated partition coefficient between ringwoodite and perovskite exhibits larger scatter. Nevertheless, the results show that the partition coefficient between ringwoodite and perovskite ($Kd=(H_2O)_\gamma/(H_2O)_{Pv}$) could be determined to be ~15 in average; this result shows that ringwoodite favors $H_2O$ 15 times more compared with perovskite.

We have already determined that the partition coefficient between olivine and wadsleyite ($Kd=(H_2O)_\beta/(H_2O)_\alpha$) was ~5 (Chen et al., 2002). Combining our previous data with our present data, the partitioning of $H_2O$ in olivine(α), wadsleyite(β), ringwoodite(γ) and perovskite(Pv) could be determined as α : β : γ : Pv = 6 : 30 : 15 : 1. Olivine is the most abundant minerals in the mantle, so the $H_2O$ partitioning among the upper mantle, between 410-520 km and 520-660 km of the mantle transition zone, and the lower mantle can be estimated as 6:30:15:1, respectively.

Because the maximum $H_2O$ solubility in wadsleyite is 3.3 wt% (e.g. Inoue et al, 1995), the possible maximum $H_2O$ storage capacities in the olivine high pressure polymorphs are as follows; ~0.7 wt% in olivine (upper mantle just above 410 km depth), ~3.3 wt% in wadsleyite (410-520 km depth), ~1.7 wt% in ringwoodite (520-660 km depth) and ~0.1 wt% in perovskite (lower mantle). With this consideration, we adopted the maximum $H_2O$ solubility in wadsleyite to discuss the maximum $H_2O$ storage capacity in the mantle. However, it was reported that the $H_2O$ solubility becomes lower with increasing temperature (e.g. Demouchy et al. 2005). The temperature in the mantle transition zone is important to estimate the $H_2O$ content.

In spite of the effect of temperature, the mantle transition zone should be a large geochemical reservoir of water in the Earth's interior, and the maximum water storage capacity in the mantle transition zone is ~4 times relative to the amount of sea water. Note that the $H_2O$ content in olivine was determined at ~13.5 GPa (just above 410 km depth), and we know that the $H_2O$ solubility in olivine increases with increasing pressure as shown in Kohlstedt et al. (1996) and Hauri et al. (2006). In the shallower mantle below 410 km depth, the $H_2O$ content in olivine should become less with

decreasing pressure.

### 3-4. Geophysical implication

Knowledge of absolute water contents in the mantle is important because hydration affects various physical properties of mantle minerals (e.g. Inoue et al, 1998; Jacobsen et al., 2004; Huang et al., 2005). Therefore, many researchers have made an effort to estimate the absolute water content in the mantle. Especially, seismological and electrical conductivity observations combined with laboratory measured values enable us to estimate the water content in the mantle. Mantle transition zone minerals, wadsleyite and ringwoodite, can accommodate significant amount of $H_2O$ (up to 2-3 wt%) in their crystal structures, so these minerals should be key minerals to contain water in the mantle.

Suetsugu et al. (2006) and Yamada et al. (2009) tried to estimate temperature anomalies and water content in the mantle transition zone just above the 660 km discontinuity beneath the Japan Islands and the Philippine Sea from tomographically determined P-velocity anomalies and the depth of the 660-km discontinuity determined by the receiver function method. The water content beneath the Philippine Sea and western Japan, where the Pacific slab is subducted, was estimated to be in the range of 1-1.5 wt% $H_2O$, and the west Philippine basin, away from the Pacific slab, did not have any significant water content. This estimated $H_2O$ content shows the relative water content anomaly with respect to average values in their study regions, because tomographically determined P-velocity anomalies were used as mentioned in Yamada et al. (2009). They observed the apparently unreasonable negative values of water content (-0.5 wt%) beneath northern Japan, and interpreted that the average $H_2O$ content could be regarded as ~0.5 wt% in the region, when it is regarded as a situation of absolutely null water (dry). Recently, Suetsugu et al. (this issue) applied the same method by using a new data set of ocean bottom geophysical observations beneath the Philippine Sea and the northwestern Pacific Ocean, and revised the water content and estimated that there was less than 0.2 wt% $H_2O$ beneath these areas. Although they mentioned that the estimated water content had an uncertainty of about 0.2-0.3 wt% $H_2O$, the average $H_2O$ content in these areas was considered to be ~0.1 wt% $H_2O$ from Figure 7 in Suetsugu et al. (this issue). Note that this estimated $H_2O$ contents reflects that in ringwoodite.

On the other hand, the electrical conductivities of wadsleyite and ringwoodite in anhydrous and hydrous forms were measured (Huang et al., 2005; Yoshino et al., 2008; Manthilake et al., 2009; Dai and Karato, 2009), and compared to the geophysical observations to estimate the water content. Though there are some arguments about the estimated water content (Karato and Dai, 2009; Yoshino and Katsura, 2009), their recent conclusions show that some water (~0.1–0.3 wt% in the Pacific) is required to explain the observed electrical conductivity (Dai and Karato, 2009). In addition, though Yoshino et al. (this issue) mentioned that the present conductivity-depth profiles in the transition zone agreed with that obtained from the geophysical observations beneath the Pacific in the case of the mantle transition zone, 0.1-0.2 wt% $H_2O$ explains the recent geophysical reference model (Shimizu et al., submitted) from Figure 6 in Yoshino et al. (this issue). Still more, Yoshino et al. (this issue) mentioned that the presence of water in the transition zone minerals is required to explain the high conductivity beneath the Philippine Sea and northeastern China (Baba et al., this issue).

In this study, we determined the partitioning of $H_2O$ among olivine high pressure polymorphs. When we apply ~0.2 wt% of the $H_2O$ content in wadsleyite in the mantle transition zone estimated by the recent electrical conductivity measurements (e.g. Dai and Karato, 2009), the estimated $H_2O$ content in the mantle is as follows; ~0.04 wt% in olivine (upper mantle), ~0.2 wt% in wadsleyite (410-520 km depth), ~0.1 wt% in ringwoodite (520-660 km depth), and ~0.007 wt% in perovskite (lower mantle). These estimated values satisfy, within the error, the recently estimated $H_2O$ content in mantle transition zone minerals (i.e. wadsleyite and ringwoodite) by different methods based on seismological and electrical conductivity observations.

Thus, the mantle transition zone should be a large geochemical reservoir of water in the Earth's mantle compared with the upper and lower mantle. Additionally, the amount of water in the mantle transition zone is ~0.3 times more relative to that of sea water, when mantle wadsleyite contains ~0.2 wt% $H_2O$.

## 4. Conclusions

We have determined the water partitioning between wadsleyite and ringwoodite, and ringwoodite and perovskite. The results are as follows; olivine : wadsleyite : ringwoodite : perovskite = 6: 30: 15 : 1. In addition, the phase boundary of olivine-wadsleyite, wadsleyite-ringwoodite, and postspinel transformations move to the

low, high, and high pressure side, respectively, with the effect of water, when we combine the present data with our previous data (Higo et al., 2001; Chen et al., 2002; Inoue et al., 2010). The resultant $H_2O$ partitioning of $[H_2O]_\alpha < [H_2O]_\beta > [H_2O]_\gamma > [H_2O]_{pv}$ is consistent with the results of the effect of water on the high pressure phase boundary of olivine.

Because the maximum $H_2O$ solubility in wadsleyite is 3.3 wt% (e.g. Inoue et al, 1995), the possible maximum $H_2O$ storage capacity in the olivine high pressure polymorphs are as follows; ~0.7 wt% in olivine (upper mantle just above 410 km depth), ~3.3 wt% in wadsleyite (410-520 km depth), ~1.7 wt% in ringwoodite (520-660 km depth), and ~0.1 wt% in perovskite (lower mantle).

When we apply ~0.2 wt% of the $H_2O$ content in wadsleyite in the mantle transition zone, the estimated $H_2O$ content through the mantle are as follows; ~0.04 wt% in olivine (upper mantle just above 410 km depth), ~0.2 wt% in wadsleyite (410-520 km depth), ~0.1 wt% in ringwoodite (520-660 km depth), and ~0.007 wt% in perovskite (lower mantle).

Thus, the mantle transition zone should contain a large water reservoir in the Earth's mantle when compared to the upper and lower mantle. Additionally, if mantle wadsleyite contains ~0.2 wt% $H_2O$ then the mantle transition zone would contain approximately one-third the $H_2O$ mass of Earth's oceans.

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**Figure captions**

Figure 1. An example of the cell assembly used in the present experiments for the wadsleyite-ringwoodite transformation.

Figure 2. (a) High pressure phase diagram of olivine high pressure polymorphs under anhydrous condition at T=1673K. The solid line represents the phase boundary from Akaogi et al. (1989) under anhydrous condition. Using this plot, the run pressures were determined.

(b) High pressure phase diagram of olivine high pressure polymorphs under hydrous condition at T=1673K. The broken line represents the phase boundary from Akaogi et al. (1989) under anhydrous condition, and the solid line represents that under hydrous condition from Inoue et al. (2010). The present results are consistent with our previous boundary of Inoue et al. (2010).

Open triangles and squares show the assemblages of the single wadsleyite phase and that of the single ringwoodite phase, respectively, and filled triangles and squares show the wadsleyite coexisting with ringwoodite, and the ringwoodite coexisting with wadsleyite, respectively. α: olivine, β: wadsleyite, γ: ringwoodite.

Figure 3. Back scattered electron image of run products (a) E1751 and (b) E1760. β: wadsleyite, γ: ringwoodite, CEn: clinoenstatite, L: liquid.

Figure 4. Back scattered electron image of run products (a) E1784 and (b) E1730. γ: ringwoodite, Pv: perovskite, L: liquid.

Fig1
Click here to download Figure(s): Fig1.pptx

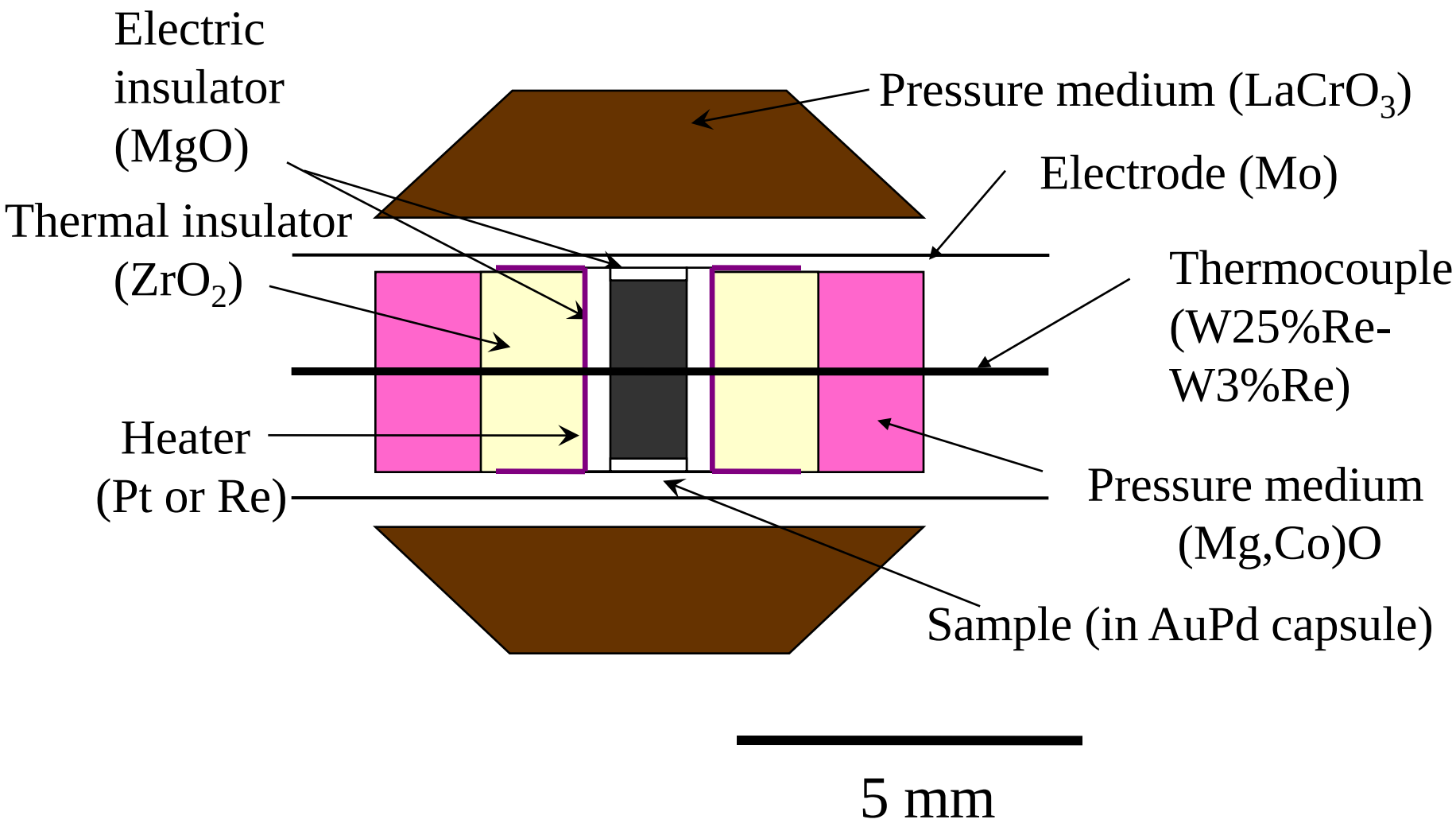


Fig. 1 Inoue et al.

Fig2a
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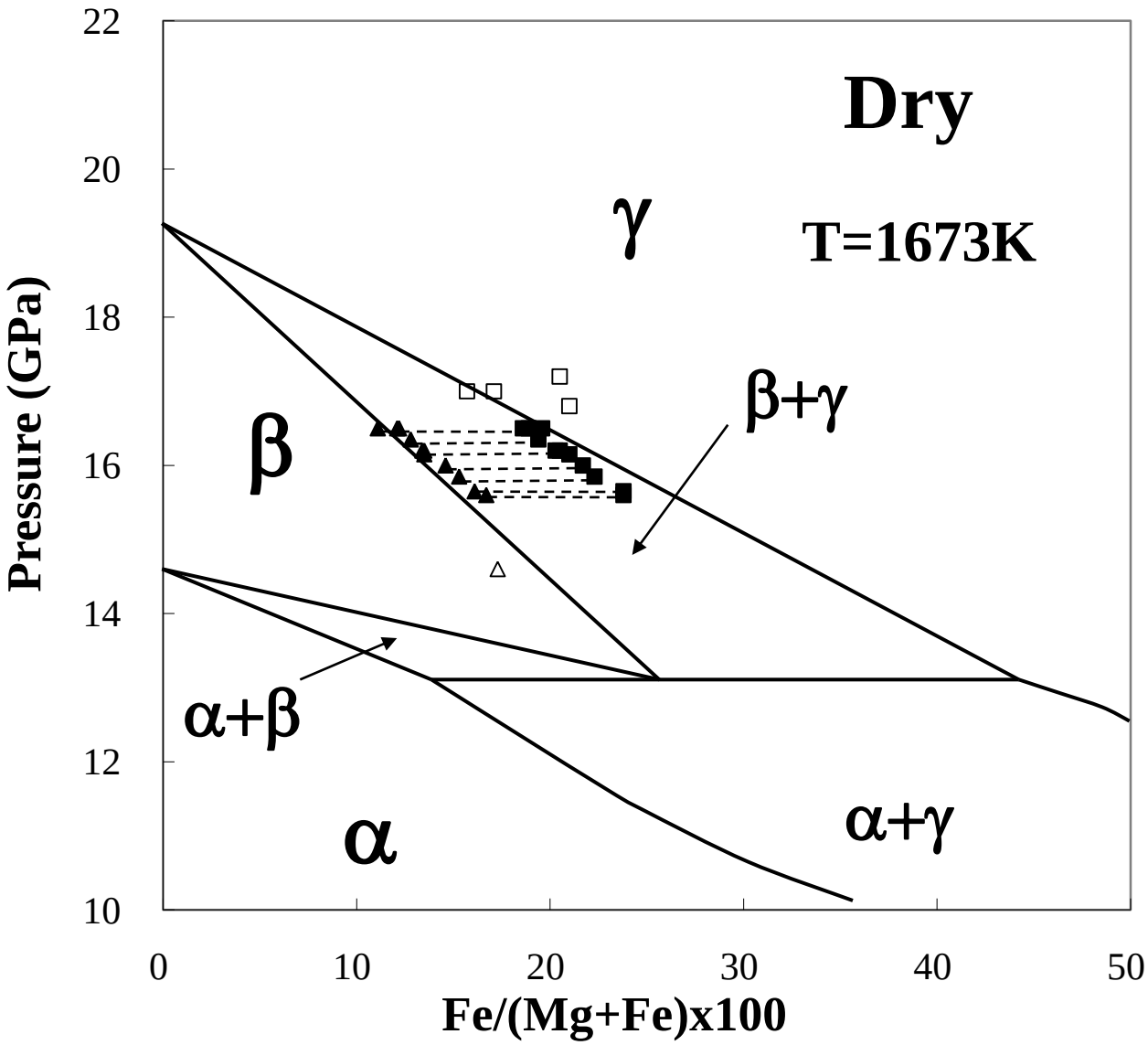


Fig. 2 (a) Inoue et al.

Fig2b
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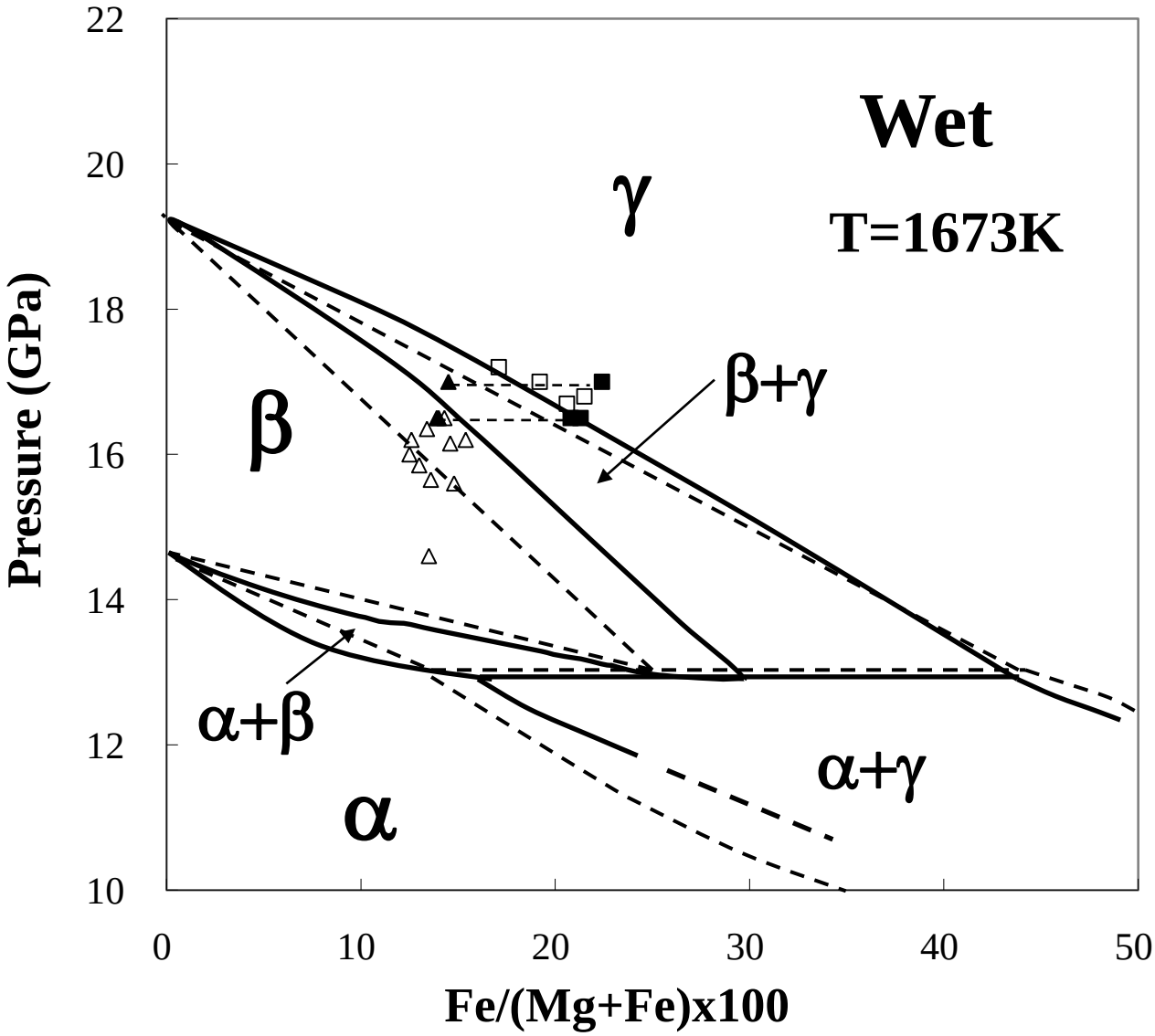


Fig. 2 (b) Inoue et al.

Fig3
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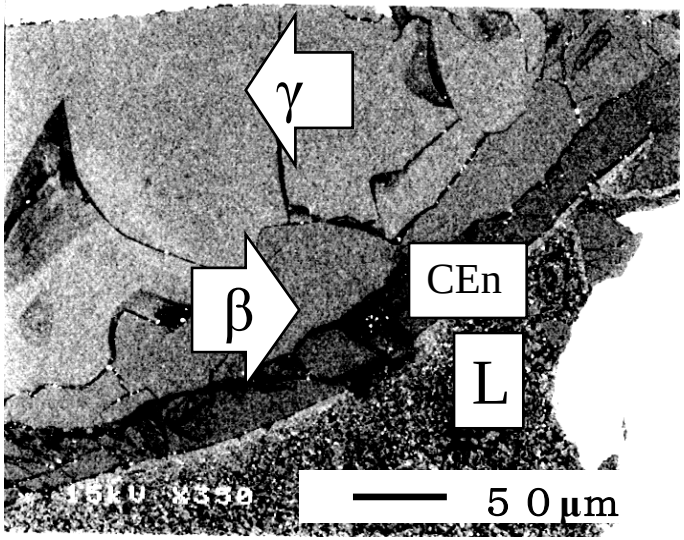
(a) E1751 WET
16.5GPa, 1673K




(b) E1760 WET
16.5GPa, 1673K

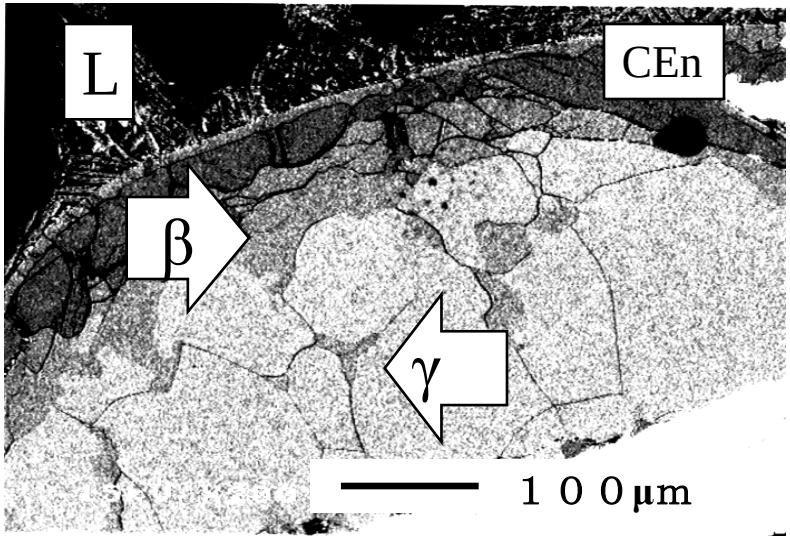



Fig. 3 Inoue et al.

Fig4
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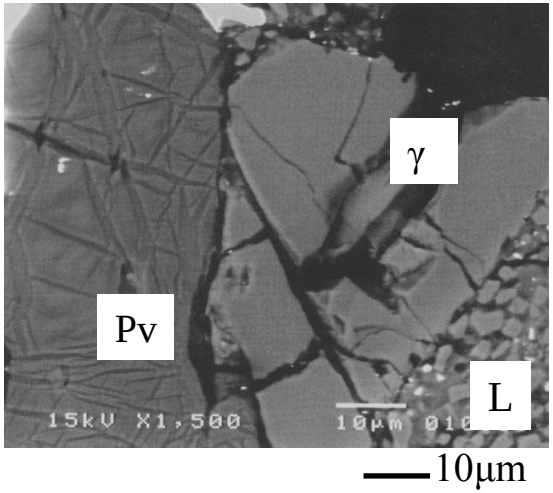
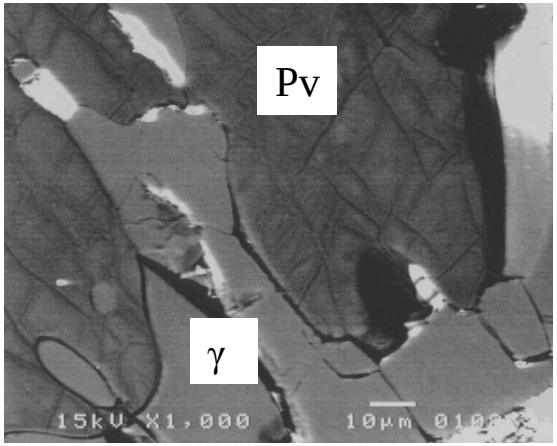
(a) E1784 WET
23.0GPa, 1873K




10μm

(b) E1730 WET
23.1GPa, 1873K




10μm

Fig. 4 Inoue et al.

**Table1**

Table 1. Chemical composition of starting material

| | Dry | Wet |
|---|---|---|
| MgO | 42.1 | 35.4 |
| FeO | 18.7 | 15.8 |
| $SiO_2$ | 39.2 | 33.0 |
| $H_2O$ | - | 15.8 |
| Total (wt%) | 100.0 | 100.0 |
| | | |
| (Mg+Fe)/Si | 2.0 | 2.0 |
| Fe/(Mg+Fe) | 0.2 | 0.2 |

Dry: $Fe_2SiO_4+8MgO+4SiO_2 \rightarrow 5(Mg_{0.8}Fe_{0.2})_2SiO_4$

Wet: $Fe_2SiO_4+8Mg(OH)_2+4SiO_2 \rightarrow 5(Mg_{0.8}Fe_{0.2})_2SiO_4+H_2O$

**Table2**

Table 2. Experimental conditions and the results (T=1673K)

| Run No. | Load (ton) | Pressure (GPa) | Time (min) | Dry | Wet |
|---|---|---|---|---|---|
| E1672 | 412 | 14.6 | 60 | β | β＋L |
| E1766 | 480 | 15.6 | 120 | β＋γ | β＋CEn＋L |
| E1748 | 470 | 15.7 | 60 | β＋γ | β＋CEn＋L |
| E1678 | 500 | 15.9 | 60 | β＋γ | β＋CEn＋L |
| E1789 | 490 | 16.0 | 60 | β＋γ | β＋L |
| E1786 | 483 | 16.2 | 90 | β＋γ | β＋CEn＋L |
| E1805 | 506 | 16.2 | 90 | β＋γ | β＋CEn＋L |
| E1744 | 505 | 16.2 | 60 | β＋γ | β＋CEn＋L |
| E1807 | 506 | 16.4 | 90 | β＋γ | β＋CEn＋L |
| E1794 | 500 | 16.5 | 90 | β＋γ | β＋L |
| E1760 | 485 | 16.5 | 90 | β＋γ | β＋γ＋CEn＋L |
| E1751 | 510 | 16.5 | 120 | β＋γ | β＋γ＋CEn＋L |
| E1788* | 485 | ~17# | 60 | γ | β＋γ+CEn＋L |
| E1758 | 508 | ~17# | 60 | γ | γ＋St＋L |
| E1738* | 520 | 16.7 | 60 | γ | γ＋L |
| E1731 | 525 | 16.8 | 60 | γ | γ＋L |
| E1683 | 550 | 17.2 | 60 | γ | γ＋L |

β: wadsleyite, γ: ringwoodite, CEn: clinoenstatite, St: stishovite, L: liquid

* Temperatures were estimated by power supply.

# These pressure should have large uncertainty.

**Table3**

Table 3. Experimental conditions and the results (T=1873K)

| Run No. | Load (ton) | Pressure (GPa) | Time (min) | Dry | Wet |
|---|---|---|---|---|---|
| E1720 | 435 | 22.9 | 60 | γ | Pv + L |
| E1767 | 435 | 22.9 | 120 | γ# | SuB+D+Mw+L |
| E1749* | 440 | 23.0 | 120 | γ# | Pv + L |
| E1759* | 440 | 23.0 | 120 | γ# | Pv+Mw+SuB+L |
| E1770 | 440 | 23.0 | 120 | Pv + Mw | Pv + Mw + L |
| E1784* | 440 | 23.0 | 20 | γ + Pv +Mw | γ + Pv + L |
| E1730 | 445 | 23.1 | 60 | γ + Pv + Mw | γ + Pv + L |
| E1787 | 445 | 23.1 | 60 | γ | Pv + L |
| E1688 | 450 | 23.2 | 60 | γ + Pv + Mw | Pv + L |
| E1695 | 450 | 23.2 | 30 | γ + Pv + Mw | γ + Pv + L |
| E1796 | 450 | 23.2 | 60 | γ# | γ+Mw+SuB+D+L |

γ：ringwoodite, Pv：perovskite, Mw：magnesiowustite, St：stishovite
SuB：superhydrous phase B, D：phase D, L：liquid
*Temperatures were estimated by power supply.
#Small amounts of magnesiowustite and stishovite exist in the run charge.

**Table4**

Table 4. Fe/(Mg+Fe) in β and γ and the partitioning (T=1673K)

| Run No. | Pressure | Dry | | | Wet | | |
|---|---|---|---|---|---|---|---|
| | | Fe/(Mg+Fe) | | | Fe/(Mg+Fe) | | |
| | (GPa) | β | γ | Kd | β | γ | Kd |
| E1672 | 14.6 | 0.173(6) | ---- | | 0.135(5) | ---- | |
| E1766 | 15.6 | 0.167(1) | 0.238(4) | 1.56 | 0.148(28) | ---- | |
| E1748 | 15.7 | 0.161(4) | 0.238(11) | 1.62 | 0.136(3) | ---- | |
| E1678 | 15.9 | 0.153(1) | 0.223(2) | 1.59 | 0.130(4) | ---- | |
| E1789 | 16.0 | 0.146(2) | 0.217(2) | 1.62 | 0.125(1) | ---- | |
| E1786 | 16.2 | 0.135(7) | 0.210(6) | 1.71 | 0.146(3) | ---- | |
| E1805 | 16.2 | 0.134(6) | 0.205(5) | 1.67 | 0.154(7) | ---- | |
| E1744 | 16.2 | 0.135(1) | 0.203(6) | 1.64 | 0.126(5) | ---- | |
| E1807 | 16.4 | 0.128(3) | 0.194(2) | 1.65 | 0.134(2) | ---- | |
| E1794 | 16.5 | 0.122(1) | 0.186(5) | 1.65 | 0.143(11) | ---- | |
| E1760 | 16.5 | 0.121(5) | 0.189(6) | 1.70 | 0.139(4) | 0.213(8) | 1.68 |
| E1751 | 16.5 | 0.111(4) | 0.196(3) | 1.95 | 0.140(5) | 0.208(3) | 1.62 |
| E1788* | ~17# | ---- | 0.157(6) | | 0.145(3) | 0.224(3) | 1.70 |
| E1758 | ~17# | ---- | 0.171(5) | | ---- | 0.192(6) | |
| E1738* | 16.7 | | N.A. | | ---- | 0.206(4) | |
| E1731 | 16.8 | ---- | 0.210(2) | | ---- | 0.215(2) | |
| E1683 | 17.2 | ---- | 0.205(2) | | ---- | 0.171(14) | |

( ): standard deviation; N.A. not analyzed; * Temperatures were estimated by power supply.

Kd = $(Fe/Mg)_{\gamma}$ / $(Fe/Mg)_{\beta}$; # These pressure should have large uncertainty.

**Table5**

Table 5. Fe/(Mg+Fe) in γ and perovskite and the partitioning (T=1873K)

| Run No. | Pressure | Dry | | | | Wet | |
|---|---|---|---|---|---|---|---|
| | | Fe/(Mg+Fe) | | | | Fe/(Mg+Fe) | |
| | (GPa) | γ | Pv | Mw | Kd | γ | Pv |
| E1784* | 23.0 | 0.199(9) | 0.086(1) | 0.342(2) | 0.38 | 0.159(1) | 0.056(3) |
| E1730 | 23.1 | 0.188(1) | N.A. | N.A. | | 0.135(2) | 0.063(4) |
| E1695 | 23.2 | 0.178(4) | 0.084(6) | N.A. | 0.42 | 0.087(2) | 0.049(3) |

( ): standard deviation; N.A. not analyzed; * Temperatures were estimated by power supply.

$Kd = (Fe/Mg)_{Pv} / (Fe/Mg)_{\gamma}$

**Table6**

Table 6. $H_2O$ partitioning between wadsleyite (β) and ringwoodite (γ)
T=1673K

| Run No. | Pressure (GPa) | $H_2O$ wt% β | $H_2O$ wt% γ | Kd |
|---|---|---|---|---|
| E1788*-1 | ~17 | 3.72 | 1.69 | 2.2 |
| E1760-1 | 16.5 | 2.28 | 1.11 | 2.05 |
| E1760-2 | 16.5 | 2.24 | 1.25 | 1.79 |
| E1751-1 | 16.5 | 1.88 | 1 | 1.88 |
| E1751-2 | 16.5 | 1.79 | 1.1 | 1.63 |
| average | | | | 1.9(2) |

* Temperature was estimated by power supply.

( ): standard deviation, $Kd=(H_2O)_\beta/(H_2O)_\gamma$

**Table7**

Table 7. $H_2O$ partitioning between ringwoodite (γ) and perovskite (Pv)
T=1873K

| Run No. | Pressure (GPa) | $H_2O$ wt% γ | $H_2O$ wt% Pv | Kd |
|---|---|---|---|---|
| E1784* | 23 | 0.76 | 0.06 | 13 |
| E1730 | 23.1 | 0.71(25) | 0.03 | 24(8) |
| E1695 | 23.2 | 0.63(11) | 0.07(3) | 9(5) |
| average | | | | 15(8) |

* Temperature was estimated by power supply.

( ): standard deviation, $Kd=(H_2O)_{\gamma}/(H_2O)_{Pv}$