



High water solubility of ringwoodite at mantle transition zone temperature

HPSTAR
906-2020

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ARTICLE INFO

Article history:

Received 18 September 2019

Received in revised form 16 November 2019

Accepted 26 November 2019

Available online xxxx

Editor: J. Brodholt

Keywords:

H₂O solubility
ringwoodite
mantle transition zone

ABSTRACT

The mantle transition zone, a potential water reservoir in the Earth's interior, is suggested to contain more than 1 wt.% of H₂O, at least locally, by the natural water-rich ringwoodite inclusion (Pearson et al., 2014) and the mineral viscosity (Fei et al., 2017). It is against the low H₂O solubility of ringwoodite (< 0.3 wt.%) at mantle transition zone temperature based on laboratory experiments (Ohtani et al., 2000). We revisited the H₂O solubility in ringwoodite at 1600–2000 K, showing that both iron-free and iron-bearing ringwoodite can store about 0.8–1.2 wt.% of H₂O under mantle transition zone conditions. Temperature has a relatively small effect on the H₂O solubility in iron-bearing system, but much larger in iron-free one. The high H₂O solubility of ringwoodite is compatible with the water-rich mantle transition zone. The relatively low values reported previously is probably due to insufficient H₂O source or unbuffered by SiO₂.

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1. Introduction

The mantle transition zone at 410–660 km depths is widely accepted as a potential water reservoir in the Earth's interior (e.g., Bercovici and Karato, 2003; Hirschmann, 2006; Tschauner et al., 2018) because its dominant minerals, wadsleyite and ringwoodite, can store up to 2.7 wt.% of H₂O in their crystal structures as hydroxyl (Kohlstedt et al., 1996). Although various estimations of H₂O contents (e.g., electrical conductivity; mineral viscosity; and seismic velocity) in the mantle transition zone range from less than 0.1 to 2 wt.% (e.g., Fei et al., 2017; Houser, 2016; Kelbert et al., 2009; Thio et al., 2016; Yoshino et al., 2008), comparisons of mineral viscosity data with geophysical observations (e.g., Fei et al., 2017) and the recently discovered ringwoodite inclusion with ~1.4 wt.% H₂O in a diamond (Pearson et al., 2014) clearly demonstrated a water-rich mantle transition zone, at least locally.

On the other hand, laboratory experiments suggested that, the H₂O solubility, which is defined as the maximum amount of H₂O that can be stored within a crystal that coexisted with hydrous melt, of wadsleyite and ringwoodite significantly decreases with increasing temperature (Demouchy et al., 2005; Litasov et al., 2011; Ohtani et al., 2000). By applying the typical geotherm, which is 1950 ~ 2000 K in the lower part of mantle transition zone from

520 to 660 km depth (Katsura et al., 2010), the solubility of H₂O in ringwoodite is only 0.3 wt.% (Ohtani et al., 2000). It would rule out the possibility of ≥ 1 wt.% H₂O in the mantle transition zone.

The above arguments imply that the H₂O solubility in ringwoodite at transition zone temperature might have been underestimated. We note that the experimental studies reporting low H₂O solubility used Fe-free Mg₂SiO₄ starting materials with 5 wt.% initial bulk H₂O content (hereafter initial H₂O) and without an SiO₂ buffer (Ohtani et al., 2000). There are two possibilities causing the underestimation: 1) Fe-bearing ringwoodite may have significantly higher H₂O solubility than Fe-free one, as the Fe effect on the H₂O solubility is currently unknown. 2) The 5 wt.% initial H₂O might be insufficient to saturate ringwoodite, as when ringwoodite coexisted only with hydrous melt and no other solid phases, there is a potential H₂O content variation in ringwoodite and melt based on the phase rule. Essentially, Fe-free ringwoodite with 2.2 and 0.8 wt.% H₂O, respectively, were synthesized at 1570 K from starting materials with 11.2 and 5 wt.% initial H₂O (Bolfan-Casanova et al., 2000; Inoue et al., 1998).

To clarify the H₂O solubility of ringwoodite under mantle transition zone conditions, we measured the H₂O contents in both Fe-free and Fe-bearing ringwoodite synthesized at 1600–2000 K with 1.5–22 wt.% initial H₂O and coexisted with akimotoite + hydrous melt. Our results show that ringwoodite can store ~0.8–1.2 wt.% H₂O at transition zone temperature, which agrees to the water-rich mantle transition zone inferred from mineral viscosity (Fei et al., 2017) and the natural inclusion (Pearson et al., 2014).

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Table 1

A list of run conditions, coexisted phases, sample thickness for FTIR, and $C_{H_2O}^{FW}$ in ringwoodite. All experiments were conducted at 23 GPa. The $C_{H_2O}^{FW}$ for each run is the average from 6–8 FTIR spectra with one standard deviation. T : temperature. t : annealing duration. Rw: ringwoodite. Aki: akimotoite. Melt: quenched crystallized melt. St: stishovite.

	Starting composition ^{*1}	Run. No.	T (K)	t (min)	Presented phases	Thickness for FTIR (μm)	$C_{H_2O}^{FW}$ (wt.%) ^{*4}	$C_{H_2O}^{RW}$ (wt.%) ^{*5}
Fo100	Mg ₂ SiO ₄ +5%H ₂ O (a)	H4775	2000	300	Rw+melt	49	0.58 (3)	0.49 (2)
		H4784L ^{*2}	1800	300	Rw+melt	49	1.33(5)	1.12 (4)
	Mg ₂ SiO ₄ +15%H ₂ O (b)	H4805	2000	300	Rw+melt	53	1.03 (4)	0.87 (4)
		H4784H ^{*2}	1800	300	Rw+Aki+melt	40	2.06 (3)	1.74 (3)
	Mg ₂ Si _{1.1} O _{4.2} +5%H ₂ O (c)	H4793	2000	300	Rw+Aki+melt	60	1.06 (6)	0.89 (5)
		H4800	1800	300	Rw+Aki+melt	54	2.03 (13)	1.71 (11)
Fo90	Mg _{1.8} Fe _{0.2} SiO ₄ +1.5%H ₂ O	H4754	2000	300	Rw+Aki+melt	72	0.25 (2)	0.18 (1)
		H4711	2000	240	Rw+Aki+melt	43	0.38 (1)	0.28 (1)
	Mg _{1.8} Fe _{0.2} SiO ₄ +5%H ₂ O	S6985	1800	40	Rw+Aki+melt	43	0.43 (2)	0.31 (2)
		H4698	2000	120	Rw+Aki+melt	47	1.19 (3)	0.87 (2)
		S7011	2000	180	Rw+Aki+melt	46	1.15 (11)	0.84 (8)
	Mg _{1.8} Fe _{0.2} SiO ₄ +15%H ₂ O	H4723	1800	180	Rw+Aki+melt	40	1.31 (8)	0.96 (6)
		H4720	1600	300	Rw+Aki+melt+st	37	1.50 (6)	1.09 (4)
		S7051	2000	240	Rw+Aki?+melt ^{*3}	43	1.11 (4)	0.81 (3)
	Fo75	Mg _{1.5} Fe _{0.5} SiO ₄ +15%H ₂ O	H4762	2000	300	Rw+melt+st	42	1.15 (7)

^{*1}: The starting composition is 100 wt.% silicate plus 1.5, 5, 15, and 22 wt.% H₂O, namely, the bulk H₂O content is 1.47 – 18.07 wt.%.

^{*2}: Two capsules with different starting materials were placed within the same assembly in this run.

^{*3}: The akimotoite in S7051 was not observed directly, nevertheless, some part of the sample in the capsule was lost during cross section preparation.

^{*4}: The $C_{H_2O}^{FW}$ is calculated with Koch-Müller and Rhede (2010) calibration, i.e., $\epsilon = 100,000 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-2}$ in Eq. (1) for Fo100 samples and $98,600 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-2}$ for Fo90 samples.

^{*5}: The $C_{H_2O}^{RW}$ is calculated with Bolfan-Casanova et al. (2018) calibration, i.e., $\epsilon = 118,500$ and $135,000 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-2}$ for Fe-free and Fe-bearing ringwoodite, respectively, and insensitive to iron content in Fe-bearing system.

2. Experimental and analytical methods

2.1. 2.1 Starting material and capsulation

MgO, SiO₂, FeO, and Mg(OH)₂ powders (> 99.9% purity), which were dried at 1370 K (MgO and SiO₂) or 400 K [FeO and Mg(OH)₂] prior to weighting, were used as starting materials. By grinding in ethanol, mixtures with bulk compositions of Mg_{1.8}Fe_{0.2}SiO₄ (Fo90), Mg_{1.5}Fe_{0.5}SiO₄ (Fo75), Mg₂SiO₄ (Fo100), and Mg₂Si_{1.1}O_{4.2} (to ensure the SiO₂ rich condition) plus 1.5 – 22 wt.% H₂O were obtained (100 wt.% silicate plus 1.5 to 22 wt.% H₂O, so the bulk H₂O contents were 1.47 – 18.1 wt.%) (Table 1). After drying in a vacuum furnace at 400 K to remove ethanol and moisture, the mixtures were sealed in Pt-Rh (5 wt.% Rh) capsules with inner diameter of 1.0 mm and outer diameter of 1.2 mm by arc welding. All the capsule lengths were carefully controlled at 1.2–1.3 mm after welding to reduce the temperature inhomogeneity and uncertainty in high-pressure experiments.

2.2. High pressure experiments

Each capsule was loaded into an MgO sleeve and placed in a LaCrO₃ furnace within a ZrO₂ thermal insulator. A Cr₂O₃-doped MgO octahedron with edge length of 10 mm was used as pressure medium (standard 10/4 cell assembly at the Bayerisches Geoinstitut). A D-type thermocouple (W₉₇Re₃-W₇₅Re₂₅) was used to measure the temperature of the capsule. The cell assembly was compressed to 23 GPa at ambient temperature using Kawai-type multi anvil apparatus and heated up to the target temperature (1600 – 2000 K) at a rate of $\sim 100 \text{ K}/\text{min}$. After annealing at the target temperature for 40–300 min, which is sufficiently long for the hydrogen equilibrium in ringwoodite (Sun et al., 2015), the assembly was quenched to room temperature by cutting off the heating power, and decompressed to ambient pressure over 15 h. A list of run conditions is given in Table 1.

2.3. Sample analyses

2.3.1. Scanning electron microscopy (SEM)

SEM analyses were performed on the cross sections of the recovered samples using the backscattering detector (BSE) with an acceleration voltage of 20 kV and the Energy-dispersive detector (EDS) accelerated with 15 kV voltage. The run products in the capsules appeared as coexisting of 100–500 μm crystals and quenched crystallized melts (Fig. 1a). SEM-EDS analyses showed the chemical compositions of the solid parts as (Mg,Fe)₂SiO₄ and (Mg,Fe)SiO₃ crystals (and SiO₂ in Run H4720).

2.3.2. Micro focus X-ray diffraction (XRD)

X-ray diffraction patterns were taken on the recovered samples using a micro focused X-ray diffractometer (Bruker AXS D8 Discover) equipped with a two dimensional solid state detector and a micro focus source of Co-K α radiation operated at 40 kV and 500 μA . Ringwoodite can be clearly identified in the solid part as the major phase and akimotoite as the secondary phase. The melt was identified as ringwoodite and phase E, both of which were probably formed by crystallization during quenching, in addition to Pt from the capsule due to the limited space resolution of the diffractometer (Fig. 1b).

2.3.3. Infrared analysis

The recovered capsules were double-side polished to a thickness of 37–72 μm (until no noisy infrared peaks at $\sim 3120 \text{ cm}^{-1}$). Fourier transformation infrared spectroscopy (FTIR) spectra were taken on the ringwoodite grains by a Bruker IFS 120 high-resolution spectrometer coupled with a Bruker IR microscope. One or two hundred scans were accumulated for each spectrum at a resolution of 2 cm^{-1} . Six to eight spectra for each sample were obtained on different regions within the same grain and different grains within the same capsule. By adjusting the aperture size (45 to 150 μm), grain boundaries, cracks, or optically visible inclusions were avoided in each analysis. Examples of the FTIR spectra were shown in Fig. 2.

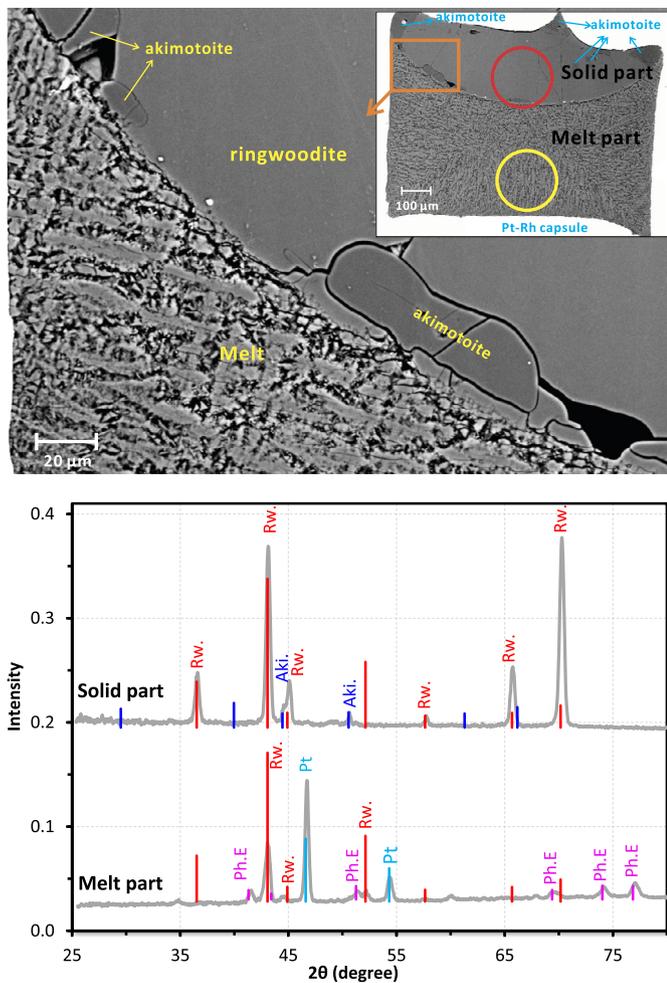


Fig. 1. Run product characterization by scanning electron microscope (SEM) and X-ray diffraction (run S7011). (a) Backscattered scanning electron microscope image. (b) X-ray diffraction patterns by micro focused diffractometer on the red (solid part) and yellow (melt part) regions in (a). Rw.: ringwoodite. Aki.: akimotoite. Ph.E: phase E, formed probably during quenching. Pt: from the capsule due to the limited space resolution of the X-ray diffractometer. (For interpretation of the colors in the figure(s), the reader is referred to the web version of this article.)

After baseline subtraction (example of baseline correction is given in Fig. 3 for various H₂O content samples), the H₂O contents in ringwoodite (C_{H₂O}^{rw}) were calculated using the Beer-Lambert law in the form,

$$C_{\text{H}_2\text{O}}^{\text{rw}} = 10^6 \times \int \frac{3A(\nu)M_{\text{H}_2\text{O}}}{\varepsilon\tau\rho} d\nu \quad (1)$$

where C_{H₂O}^{rw} is the H₂O content in wt. ppm, A(ν) is the infrared absorption at wavenumber ν, M_{H₂O} is the molar weight of H₂O (18.02 g/mol), ε is the infrared absorption coefficient [ε = 100,000 and 98,600 L·mol⁻¹·cm⁻² for Fe-free and Fe-bearing samples, respectively (Koch-Müller and Rhede, 2010)], τ is sample thickness (normalized to 1 cm in Fig. 2), and ρ is the density [3650 g·L⁻¹ (Jacobsen et al., 2004)]. The integration was performed for the wavenumber range of 2400 to 4000 cm⁻¹.

Note that Koch-Müller and Rhede (2010)'s FTIR calibration is based on secondary ion mass spectrometry (SIMS) data. Recently, Bolfan-Casanova et al. (2018) reported ε = 118,500 L·mol⁻¹·cm⁻² for Fe-free ringwoodite and 135,000 L·mol⁻¹·cm⁻² for Fe-bearing ringwoodite based on elastic recoil detection analysis (ERDA). By using Bolfan-Casanova et al. (2018)'s calibration, the C_{H₂O}^{rw} values will be lower by 16% (Fe-free) or 27% (Fe-bearing) as listed in Table 1 for comparison.

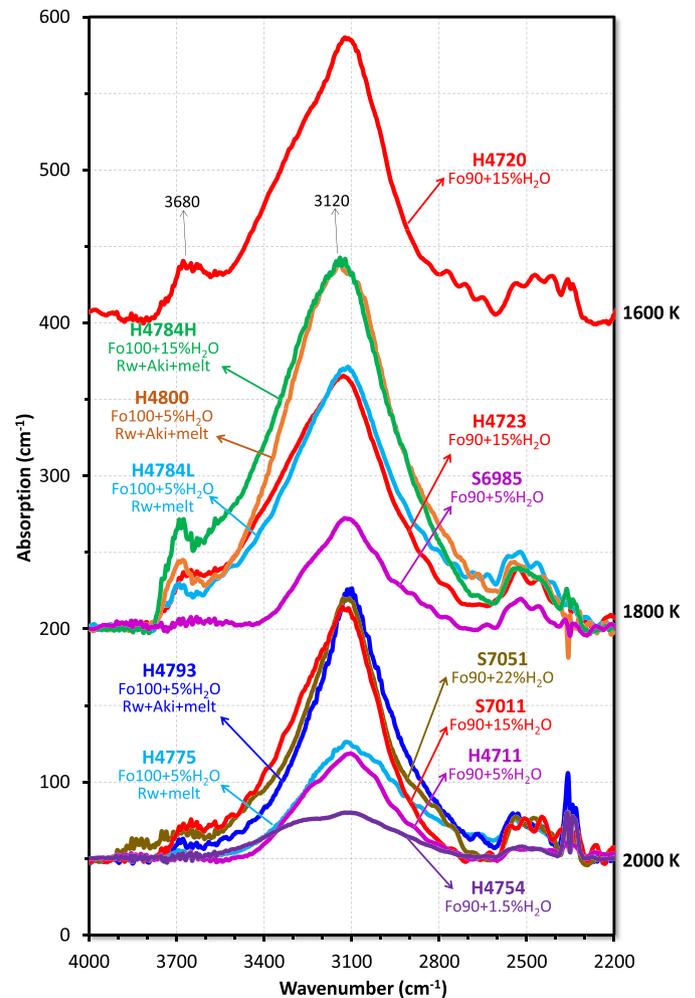


Fig. 2. Examples of FTIR spectra after baseline subtraction and thickness normalization to 1 cm. The absorption at ~2340 cm⁻¹ is caused by CO₂ in the atmosphere. All the spectra were vertically shifted for visibility.

2.3.4. EPMA analysis

The major components (MgO, SiO₂, and FeO) in the run products were obtained by the JEOL JXA-8200 electron probe microanalyzer (EPMA) with a wavelength-dispersive spectrometer (WDS) operated with an acceleration voltage of 15 kV, a beam current of 15 nA, and a counting time of 20 s. The detailed compositions were listed in Table 2 and Table 3 for ringwoodite and coexisted melt, respectively. The mass fraction of each component by EPMA would be affected by the Fe³⁺/Fe²⁺ ratio, however, the atomic (Mg+Fe)/Si and Fe/(Fe+Mg) ratios listed in Table 2 and Table 3 should be independent from Fe³⁺/Fe²⁺ ratio.

The Fe content in Pt-Rh capsule was also examined by EPMA. That was about 2 wt.% within 1 - 2 μm away from the inner wall of the capsule, and decreased to < 0.2 wt.% at ~6 μm away from the inner wall. Therefore, the Fe loss into the capsules was completely negligible.

3. Results

3.1. Infrared spectra

The FTIR spectra obtained in different regions of each capsule are very similar, indicating very homogeneous H₂O distribution and therefore homogeneous temperature distribution within the capsule. The absorptions appear as a very broad band from 2600 to 3800 cm⁻¹ and small bands at 2450, 2530, and 2660 cm⁻¹

Table 2
Chemical composition of the recovered ringwoodite analyzed by electron microprobe. The data in parentheses are one standard deviation of the N analyzed points for each sample. The atomic number is normalized to O = 24. The Fe is assumed to be ferrous although up to 15~18% of total Fe can be ferric (McCammon et al., 2004).

Run. No.	Number of points	MgO (wt.%)	SiO ₂ (wt.%)	FeO (wt.%)	Total (wt.%)	Mg (atomic)	Si (atomic)	Fe (atomic)	(Mg+Fe)/Si atomic ratio	Fe/(Mg+Fe) atomic ratio
H4775	14	55.81 (26)	42.29 (37)	–	98.10 (61)	11.901 (32)	6.049 (16)	–	1.967 (11)	–
H4784L	11	55.65 (80)	42.27 (41)	–	99.06 (48)	11.767 (139)	5.996 (70)	–	1.963 (46)	–
H4805	12	55.46 (35)	42.60 (20)	–	98.06 (51)	11.819 (28)	6.091 (14)	–	1.940 (9)	–
H4784H	12	55.03 (21)	42.56 (30)	–	97.63 (40)	11.777 (41)	6.110 (22)	–	1.928 (14)	–
H4793	13	55.23 (18)	42.30 (16)	–	97.56 (20)	11.835 (34)	6.081 (16)	–	1.946 (11)	–
H4800	19	54.69 (24)	42.80 (16)	–	97.52 (25)	11.705 (38)	6.145 (19)	–	1.905 (12)	–
H4754	10	50.49 (52)	40.03 (40)	8.31 (41)	98.82 (104)	11.132 (67)	5.921 (31)	1.027 (46)	2.054 (21)	8.45 (37)%
H4711	12	50.88 (29)	41.17 (13)	7.16 (40)	99.20 (29)	10.948 (54)	5.943 (20)	0.778 (43)	1.973 (12)	6.63 (37)%
S6985	12	50.36 (28)	40.97 (24)	8.67 (25)	100.01 (35)	10.802 (59)	5.895 (28)	0.939 (26)	1.992 (18)	8.00 (23)%
H4698	15	50.13 (39)	41.16 (23)	7.27 (35)	98.56 (35)	10.853 (78)	5.977 (28)	0.795 (38)	1.949 (19)	6.82 (34)%
S7011	13	52.05 (30)	41.35 (24)	5.44 (47)	98.84 (29)	11.190 (68)	5.963 (24)	0.590 (51)	1.976 (14)	5.01 (43)%
H4723	21	51.52 (23)	40.95 (20)	6.33 (13)	98.79 (23)	11.114 (46)	5.926(26)	0.689 (14)	1.992 (17)	5.84 (11)%
H4720	15	49.70 (36)	41.48 (27)	6.96 (32)	98.13 (27)	10.782 (71)	6.037 (34)	0.762 (36)	1.912 (21)	6.60 (31)%
S7051	17	53.95 (67)	41.01 (61)	3.55 (9)	98.52 (20)	11.596 (160)	5.913 (79)	0.386 (9)	2.027 (54)	3.22 (9)%
H4762	12	47.63 (13)	40.22 (12)	11.77 (20)	99.62 (32)	10.345 (21)	5.860 (13)	1.290 (20)	1.986 (8)	11.09 (17)%

Table 3
Chemical composition of the melt analyzed by electron microprobe. The data in parentheses are one standard deviation of the N analyzed points for each sample. The atomic number is normalized to O = 24. The Fe is assumed to be ferrous.

Run. No.	Number of points	MgO (wt.%)	SiO ₂ (wt.%)	FeO (wt.%)	Total (wt.%)	Mg (atomic)	Si (atomic)	Fe (atomic)	(Mg+Fe)/Si atomic ratio	Fe/(Mg+Fe) atomic ratio
H4775	9	43.3 (9)	27.6 (24)	–	70.9 (28)	12.96 (47)	5.52 (24)	–	2.35 (18)	–
H4784L	12	42.2 (15)	19.1 (7)	–	61.4 (18)	14.91 (22)	4.53 (11)	–	3.30 (13)	–
H4805	13	42.7 (9)	33.8 (8)	–	76.5 (14)	11.64 (17)	6.18 (9)	–	1.89 (5)	–
H4784H	15	41.1 (11)	25.7 (15)	–	66.9 (9)	13.04 (48)	5.47 (24)	–	2.39 (19)	–
H4793	5	47.6 (14)	35.4 (37)	–	83.1 (42)	12.03 (64)	5.98 (32)	–	2.02 (22)	–
H4800	11	37.8 (16)	25.2 (11)	–	63.2 (13)	12.65 (48)	5.66 (24)	–	2.24 (18)	–
H4754	8	34.0 (14)	22.3 (12)	19.7 (19)	76.0 (30)	10.89 (39)	4.79 (16)	3.53 (28)	3.01 (17)	24.5 (19)%
H4711	11	37.1 (12)	34.2 (8)	16.5 (4)	87.7 (4)	9.33 (29)	5.76 (13)	2.10 (6)	1.98 (9)	18.4 (7)%
S6985	14	39.1 (1)	27.1 (4)	12.3 (3)	78.5 (6)	11.08 (8)	5.14 (4)	1.76 (4)	2.50 (3)	13.7 (3)%
H4698	14	36.8 (8)	32.2 (5)	10.8 (2)	79.7 (11)	10.02 (14)	5.88 (7)	1.48 (2)	1.96 (5)	12.9 (2)%
S7011	15	38.3 (7)	31.2 (11)	10.9 (3)	80.5 (12)	10.40 (17)	5.68 (11)	1.49 (6)	2.10 (8)	12.6 (4)%
H4723	13	36.8 (7)	26.0 (8)	13.7 (3)	76.5 (7)	10.75 (23)	5.11 (13)	2.02 (5)	2.50 (11)	15.8 (3)%
H4720	10	34.6 (7)	20.4 (6)	17.9 (4)	72.8 (7)	11.01 (18)	4.34 (10)	2.87 (7)	3.20 (11)	20.7 (5)%
S7051	14	39.9 (11)	32.1 (8)	9.7 (3)	81.6 (16)	10.60 (15)	5.72 (8)	1.30 (6)	2.08 (6)	10.9 (5)%
H4762	10	29.9 (8)	26.8 (5)	27.3 (4)	84.0 (7)	8.29 (18)	4.99 (8)	3.83 (8)	2.43 (7)	31.6 (8)%

(Fig. 2). The absorption band at 3680 cm⁻¹ appears at C_{H₂O}^{rw} > ~1.0 wt.%, and is typically sharper in Fe-free ringwoodite than Fe-bearing one. These features agree with those reported previously (e.g., Bolfan-Casanova et al., 2018; Keppler and Bolfan-Casanova, 2006; Panero et al., 2013; Pearson et al., 2014; Smyth et al., 2003). The absorptions at 3120 cm⁻¹ appear as smooth peaks without noise, indicating no photon saturation in FTIR analyses.

3.2. C_{H₂O}^{rw} in the run products

For Fe-bearing system, the initial H₂O and Fe contents in the starting materials vary from 1.5 to 22% and Fo75 to Fo90, respectively. In the run products, with increasing temperature from 1600 to 2000 K, the C_{H₂O}^{rw} systematically decreases from 1.50 to ~1.15 wt.% for starting material of Fo90 + 15% H₂O. By reducing the initial H₂O from 15 to 1.5%, C_{H₂O}^{rw} decreases almost proportionally. However, the C_{H₂O}^{rw} from 15 and 22 wt.% initial H₂O runs are nearly identical at 2000 K (Table 1, Fig. 4). Adding more Fe in the starting material (Fo75) does not change C_{H₂O}^{rw} significantly at 2000 K (Fig. 4, 5). Note that as mentioned in section 2.3, the above C_{H₂O}^{rw} values are lowered by 27% for Fe-bearing system based on Bolfan-Casanova et al. (2018) FTIR calibration as listed in Table 1.

For Fe-free system, three sets of experiments with different starting materials were performed: run a) Mg₂SiO₄ + 5 wt.% H₂O, run b) Mg₂SiO₄ + 15 wt.% H₂O, and run c) Mg₂Si_{1.1}O_{4.2} + 5 wt.% H₂O (SiO₂ rich to ensure the coexistence of three phases), and the run products appeared as coexisting of: a) ringwoodite + melt, b) ringwoodite + melt + (akimotoite), and c) ringwoodite + akimo-

toite + melt, respectively. The products of run (c) show C_{H₂O}^{rw} = 2.03 wt.% at 1800 K and 1.06 wt.% at 2000 K [or 1.71 and 0.89 wt.% with Bolfan-Casanova et al. (2018) FTIR calibration], which are essentially the same as those in run (b), but considerably higher than those in run (a) (1.33 wt.% at 1800 K and 0.58 wt.% at 2000 K) (Table 1, Fig. 4).

4. Discussion

4.1. (Mg+Fe)/Si ratio and hydrogen incorporation in ringwoodite

H₂O is incorporated into (Mg,Fe)₂SiO₄ polymorphs as protons in Mg (and Fe) and/or Si sites. In general, a proportion of protons in Mg and Si sites can be estimated based on the deviation of the (Mg+Fe)/Si atomic ratio (Mg/Si ratio in Fe-free system) from the ideal formula. This ratio in wadsleyite significantly decreases with increasing H₂O content, therefore, the majority of protons are supposed to be in Mg sites (Demouchy et al., 2005; Inoue et al., 1995) (Fig. 6). In the case of ringwoodite, the Mg/Si ratios for our and for Ohtani et al. (2000)'s high-C_{H₂O}^{rw} and Fe-free samples are obviously higher than those of wadsleyite, and are plotted around the line where protons are incorporated in Mg and Si sites with a ratio of about 2:1 (3:1 if only use the data from this study) (Fig. 6). It agrees with neutron diffraction experiments (Purevjav et al., 2014), which suggested simultaneous hydration of Mg and Si sites in ringwoodite. The Hydration process is thus written as,



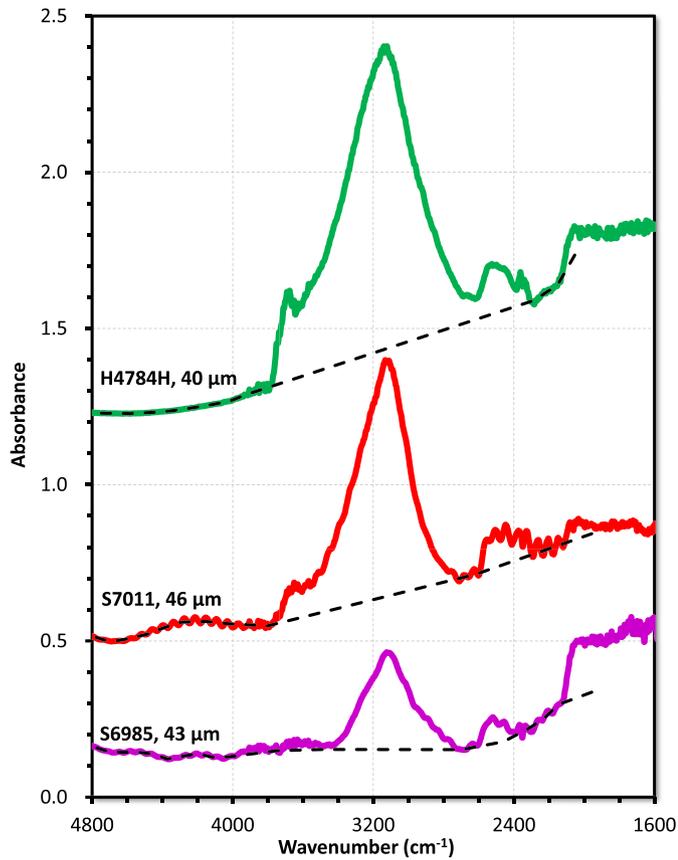


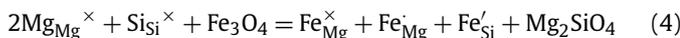
Fig. 3. Examples of baseline subtractions for FTIR spectra with various absorbances, corresponding different H₂O contents. The spectra were vertically shifted for visibility.



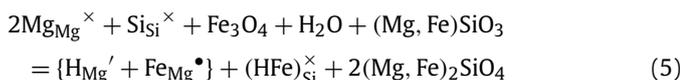
The reaction (2) occurs 4–6 times more than that of (3) and the ratio of [(2H)_{Mg}[×]] and [(4H)_{Si}[×]] is expected to be 4~6:1. [Here Kröger-Vink (1956) notation is used for the description of defect chemistry, e.g., (2H)_{Mg}[×] means two protons in the Mg site with neutral charge, Fe_{Si}['] and Fe_{Mg}[•] indicate Fe ions substitute the Si and Mg sites, with effective charge of −1 and +1, respectively, and square brackets [A] denote the concentration of the species A.]

In contrast, the Fe-free samples with relatively low C_{H₂O}^{rw} (< ~1.0 wt.%) (This study; Bolfan-Casanova et al., 2018; Ohtani et al., 2000) generally follow the pure Mg site substitution, which means that the reaction (2) is probably more preferred when the C_{H₂O}^{rw} is low. The substitution mechanism of reaction (3) occurs with increasing of C_{H₂O}^{rw}.

About 15–18% of total Fe is ferric in hydrous ringwoodite based on Mössbauer spectroscopy (McCammon et al., 2004). Because both ringwoodite and magnetite have the spinel structure, a certain proportion of (Mg,Fe)₂SiO₄ should be substituted by Fe₃O₄,



The Fe³⁺ related hydration process is thus considered as,



This hydration process may cause slightly higher (Mg+Fe)/Si ratio than Fe-free ringwoodite although such tendency was unclear in Fig. 6 due to the large scattering of data points for Fe-bearing samples.

4.2. H₂O solubility in ringwoodite

4.2.1. Fe-bearing system

The C_{H₂O}^{rw} in Fe-bearing ringwoodite with 15 and 22 wt.% initial H₂O are identical, and considerably higher than those with 1.5–5 wt.% initial H₂O (Fig. 4). Clearly, the runs with 15–22 wt.% initial H₂O should represent the H₂O solubility in ringwoodite since C_{H₂O}^{rw} is independent from initial H₂O content. Ringwoodite from the experiments with 1.5–5 wt.% initial H₂O should be undersaturated. The H₂O solubility is thus 1.15–1.50 wt.% at 1600 to 2000 K (0.84–1.09 wt.% based on Bolfan-Casanova et al., 2018's FTIR calibration). This value is comparable with that reported by Fei et al. (2017) at 1800 K, who used free water as H₂O source (namely very high but unknown initial H₂O). In contrast, it is 1.5–3.0 times higher than those reported previously who used only 3–5 wt.% initial H₂O (Bolfan-Casanova et al., 2018; Kawamoto et al., 1996; Smyth et al., 2003) (Fig. 4). One may attribute this difference to the various analytical methods adopted in measuring the H₂O contents [i.e. FTIR with various calibrations, ERDA, and SIMS]. As demonstrated in Bolfan-Casanova et al. (2018), however, only Paterson (1982)'s FTIR calibration, namely, Smyth et al. (2003) may have significantly underestimated the H₂O solubility, whereas the other methods should have given comparable results (Fig. 4). Essentially, as demonstrated by our FTIR spectra (Fig. 2), C_{H₂O}^{rw} is limited by the initial H₂O if it is low.

In the view of thermodynamics, although three phases coexisted (ringwoodite + akimotoite + melt), the composition of each phase (e.g. C_{H₂O}^{rw} in ringwoodite) should be fixed at a given pressure and temperature condition only in the three-component system (e.g. Demouchy et al., 2005). Since there are four/five components in the Fe-bearing experiments [MgO + SiO₂ + H₂O + FeO (+Fe₂O₃)], there should be one or two more freedom. It is thus reasonable that C_{H₂O}^{rw} is initial- H₂O dependent when it is below the solubility. As experimentally observed, if the initial H₂O is low (1.5 ~ 5% H₂O), C_{H₂O}^{rw} systematically increases with increasing initial H₂O content. When the initial H₂O is 15 ~ 22%, C_{H₂O}^{rw} reaches the solubility value and therefore it becomes independent from initial H₂O content.

4.2.2. Fe-free system

There are three components (MgO-SiO₂-H₂O) in the Fe-free system. As far as three phases coexist, all the thermodynamic parameters of the system should be fixed at a given pressure and temperature condition. Namely, no matter how much H₂O is added in the starting material, the C_{H₂O}^{rw} should remain unchanged when ringwoodite, akimotoite, and melt coexist. This turned out to be true in our experiments (Fig. 4, Table 1), i.e., the C_{H₂O}^{rw} in runs (b) and (c) are essentially the same, for which the bulk compositions of the starting materials are located within the ringwoodite-akimotoite-melt triangle in the compositional diagram (Fig. 7). Therefore, the H₂O solubility in Fe-free ringwoodite should be ~2.0 and ~1.0 wt.% at 1800 and 2000 K, respectively, based on Koch-Müller and Rhede (2010) calibration, or ~1.7 and 0.9 wt.%, respectively, if use the relatively larger FTIR absorption coefficient reported by Bolfan-Casanova et al. (2018).

In contrast, the C_{H₂O}^{rw} obtained in runs (a) is only 1.33 and 0.58 wt.% at 1800 and 2000 K, respectively (0.49 and 1.12 wt.% based on Bolfan-Casanova et al.'s calibration), whereas Ohtani et al. (2000) obtained C_{H₂O}^{rw} of 0.2~0.3 wt.% at 1950–2070 K. These values are considerably lower than the H₂O solubility determined by runs (b) and (c), and this difference is not related to the FTIR calibration methods because the infrared absorptions are clearly different as shown in Fig. 2. Since Mg₂SiO₄ + 5% initial H₂O was used as starting material and only two phases (ringwoodite + melt) coexisted in those low-C_{H₂O}^{rw} experiments, there should be one more freedom additional to pressure and temperature in

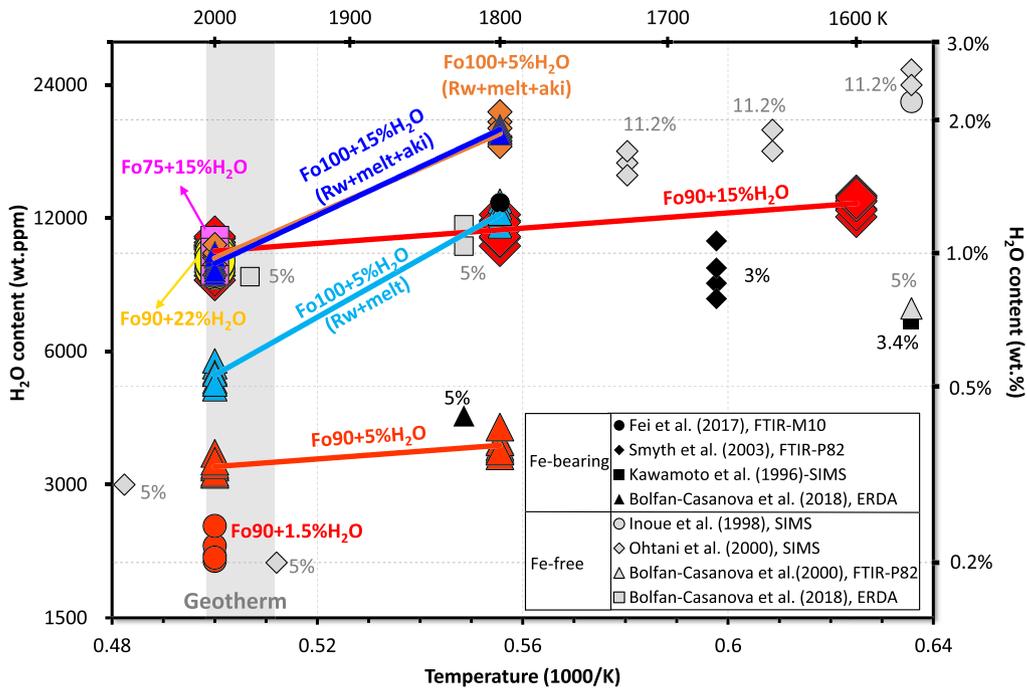


Fig. 4. Temperature dependence of H₂O content or solubility in ringwoodite. The data sets labeled with Fo100+5%H₂O (Mg₂Si_{1.1}O_{4.2}), Fo100+15%H₂O, Fo90+22%H₂O, Fo90+15%H₂O, and Fo75+15%H₂O should represent the H₂O solubility in ringwoodite. Each data point from this study is C_{H₂O}^{TW} from one single FTIR spectrum based on the average of Koch-Müller and Rhede (2010) and Bolfan-Casanova et al. (2018) calibrations. The percentages next to the data points are the initial H₂O contents in the starting materials. The geotherm in the lower mantle transition zone is taken from Katsura et al. (2010). SIMS: secondary ion mass spectrometry. FTIR-P82: FTIR with Paterson (1982) calibration. FTIR-M10: FTIR with Koch-Müller and Rhede (2010) calibration. ERDA: elastic recoil detection analysis (Bolfan-Casanova et al., 2018). Although more data were reported in Bolfan-Casanova et al. (2018) and Smyth et al. (2003), only C_{H₂O}^{TW} for ringwoodite that coexisted with melts were shown in the figure since C_{H₂O}^{TW} from other runs cannot represent the H₂O solubility.

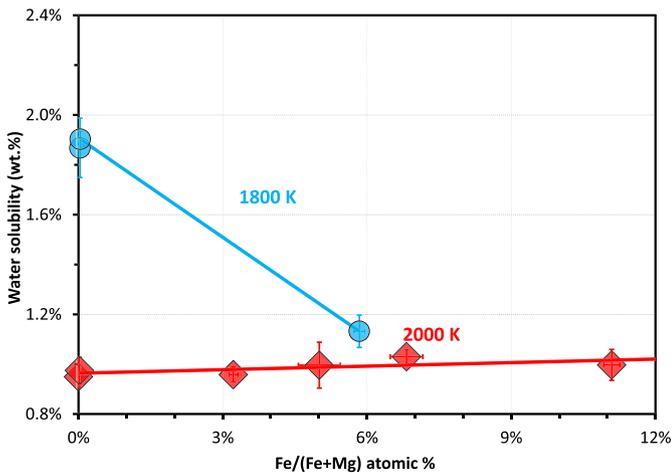


Fig. 5. Fe content dependence of H₂O solubility in ringwoodite based on the average of Koch-Müller and Rhede (2010) and Bolfan-Casanova et al. (2018) calibrations. Although the Fe/(Fe+Mg) atomic ratio in the starting material for Fe-bearing system was 10% or 25%, that in ringwoodite was less than 11% since Fe prefers to participate into melt rather than solid.

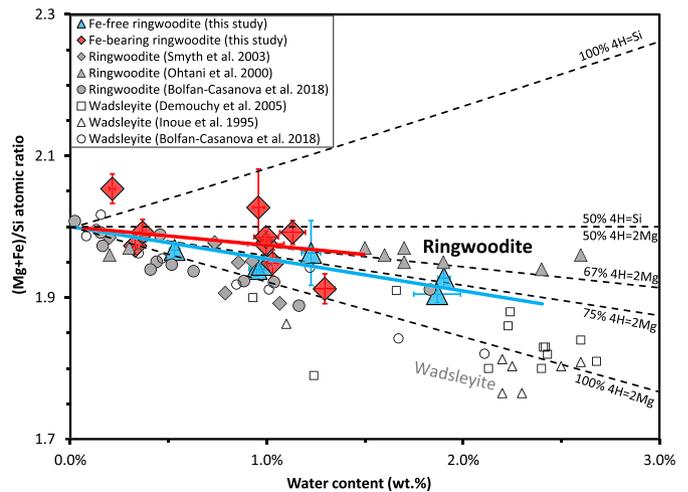


Fig. 6. (Mg+Fe)/Si atomic ratio in ringwoodite as a function of H₂O content from the average of Koch-Müller and Rhede (2010) and Bolfan-Casanova et al. (2018) calibrations. The ratio in wadsleyite is also shown for comparison. The interception of fitting lines on vertical axis is set to (Mg+Fe)/Si = 2.0. The dash lines represent the theoretical calculations with 100% proton following (4H)₂MgSiO₄ substitution mechanism, 100% following Mg₂(4H)₂SiO₄ substitution mechanism, 50:50, 67:33, and 75:25 of (4H)₂MgSiO₄ and Mg₂(4H)₂SiO₄ substitution mechanisms. The samples of Inoue et al. (1998), Ohtani et al. (2000), and Demouchy et al. (2005) are all Fe-free, whereas Bolfan-Casanova et al. (2018) of both Fe-free and Fe-bearing systems.

the MgO-SiO₂-H₂O system. Namely, those samples may not represent the H₂O solubility in Fe-free ringwoodite. Because run (a) is not buffered by silica-rich phases such as akimotoite or stishovite, the Mg/Si ratio is thus slightly higher, which could be the reason for the low C_{H₂O}^{TW} as far as the majority of protons is stored in Mg vacancies as discussed above. It is speculated that the melt composition varies with initial H₂O in the ringwoodite + melt two-phase region of the phase diagram, leading to various C_{H₂O}^{TW} with the initial composition (Fig. 7). By adding either more H₂O or more SiO₂ in the Mg₂SiO₄ + 5% H₂O system, the bulk composition

would be located in the ringwoodite + akimotoite + melt three-phase region and then the ringwoodite would be H₂O-saturated.

Quite recently, Bolfan-Casanova et al. (2018) reported C_{H₂O}^{TW} = 0.89 wt.% at 1970 K in Fe-free ringwoodite. It is identical to the C_{H₂O}^{TW} obtained in run (b) and (c) by considering the 16% lower of C_{H₂O}^{TW} with Bolfan-Casanova et al. (2018) calibration even though Mg₂SiO₄ + 5% initial H₂O were used in their experiments. It is

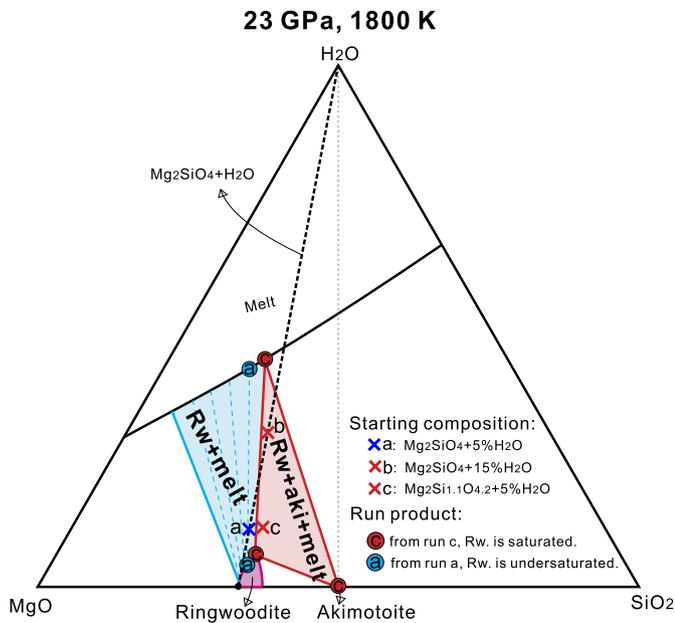


Fig. 7. Ternary phase diagram in the MgO-SiO₂-H₂O system at 23 GPa, 1800 K based on the runs H4784L, H4784H, and H4800. The red and blue area represent the three-phase (ringwoodite + akimotoite + melt) and two-phase (ringwoodite + melt) coexisting regions, respectively. The H₂O concentrations in the melt phases were estimated from initial H₂O contents in the starting materials and melt fractions of the run products. The cross and circle symbols denote the compositions of the starting materials and run products, respectively.

actually not against our results because their brucite was CO₂-contaminated, therefore, the starting material could be actually slightly SiO₂ rich.

4.2.3. Temperature and Fe content dependences of H₂O solubility

Temperature has significant effect on the H₂O solubility in Fe-free ringwoodite. With increasing temperature from 1800 to 2000 K, the H₂O solubility decreases by ~50%. In contrast, the H₂O solubility is less sensitive to temperature in Fe-bearing system. From 1600 to 2000 K, the H₂O solubility decreases from 1.50 to 1.15 wt.% (1.09 to 0.84 wt.% based on Bolfan-Casanova et al.'s calibration) (Fig. 4; Table 1). Note that a crossover of Fo90 and Fo100 lines occurs at ~1950 K (Fig. 4), however, it is probably caused by experimental uncertainty because the difference of H₂O solubility between Fe-free and Fe-bearing samples are less than ~15% at 2000 K (1.03~1.06 vs. 1.11~1.19 wt.%) (Table 1).

The H₂O solubility is nearly independent from Fe content at 2000 K, whereas that at 1800 K in Fe-bearing ringwoodite is much lower than Fe-free system (Fig. 4, Fig. 5). Namely, Fe-free ringwoodite can store more H₂O than Fe-bearing one at < 2000 K. Since silicate melt and H₂O are miscible under mantle transition zone conditions (Bureau and Keppler, 1999; Demouchy et al., 2005; Kawamoto et al., 2004), the H₂O solubility in ringwoodite is controlled by the H₂O activity in the coexisting hydrous melt (e.g., Demouchy et al., 2005; Keppler and Bolfan-Casanova, 2006). By adding Fe₂SiO₄ component, the melt fraction may increase slightly because the melting temperature of (Mg,Fe)₂SiO₄ decreases with increasing Fe/(Mg+Fe) ratio. As a result, the H₂O activity in melt decreases, which causes the lower H₂O solubility in Fe-bearing ringwoodite.

Additionally, variation of oxygen fugacity (f_{O_2}) may affect the Fe³⁺/Fe²⁺ ratio in Fe-bearing ringwoodite. Based on Mössbauer spectroscopy analysis (McCammon et al., 2004), however, Fe³⁺/Fe²⁺ ratio is independent from $C_{H_2O}^{TW}$, namely, the H₂O solubility should be independent from f_{O_2} as well. This is also proved

by the identical $C_{H_2O}^{TW}$ obtained in this study without controlling f_{O_2} with that in Fei et al. (2017) buffered by Re foils (Fig. 4).

4.3. Water in the mantle transition zone

Wadsleyite and ringwoodite are the dominant minerals in the upper (410-520 km depth) and lower (520-660 km depth) part of the mantle transition zone, respectively (e.g., Ringwood, 1991). The H₂O solubility of wadsleyite at 1850-1900 K (upper mantle transition zone geotherm) has been estimated to be 0.8-1.1 wt.% (Demouchy et al., 2005; Kawamoto et al., 1996; Litasov et al., 2011; Sun et al., 2018), (Fig. 4). Meanwhile, even at 1950-2000 K, corresponding to the lower mantle transition zone geotherm (Katsura et al., 2010), 1.1~1.2 wt.% H₂O based on Koch-Müller and Rhede's calibration, or 0.8~0.9 wt.% H₂O based on Bolfan-Casanova et al.'s calibration, can be stored within the crystals of iron-bearing ringwoodite, which is 3-6 times higher than that reported previously (Ohtani et al., 2000). Namely, both the upper and lower mantle transition zone can store about 0.8~1.2 wt.% H₂O.

Of course H₂O solubility of minerals does not represent the actual H₂O content in the mantle transition zone. The question is whether the mantle transition zone is H₂O rich or not. Based on the comparison of magnetotellurically-interpreted electrical conductivity with the laboratory-measured conductivity of wadsleyite and ringwoodite, it has been proposed that the mantle transition zone contains < 0.1 ~ 1.0 wt.% H₂O (Huang et al., 2005; Karato, 2011; Kelbert et al., 2009; Yoshino et al., 2008). However, due to the difficulties of conductivity measurements, the estimated H₂O contents in the mantle transition zone by different groups range by nearly one order of magnitude. Additionally, most of the H₂O-related conductivity measurements only focus on the free-proton controlled conduction mechanism at low temperature regime (typically < 1500 K). It should be inappropriate for estimation of H₂O content in the mantle transition zone due to the conduction mechanism transitions at higher temperatures (Yoshino et al., 2008).

From seismic data (e.g., Houser, 2016; Meier et al., 2009), a relatively dry mantle transition zone (< 0.6 wt.% H₂O) has been proposed based on the reduction of sound velocity by the hydration of wadsleyite and ringwoodite (Jacobsen et al., 2004; Mao et al., 2008). Nevertheless, recent experiments (Buchen et al., 2018; Schulze et al., 2018) demonstrated that the elasticity of both wadsleyite and ringwoodite are insensitive to H₂O contents under mantle transition zone conditions, therefore, seismic observations would be unable to tell the hydration states in the mantle transition zone.

Since the viscosity of nominally anhydrous minerals is lowered by hydration, Fei et al. (2017) investigated the viscosity contrast between ringwoodite and bridgmanite and concluded that the mantle transition zone should contain ≥ 1.0 wt.% H₂O to fit the geophysically interpreted mantle viscosity profiles. According to the high H₂O solubility reported here, ringwoodite in the mantle transition zone can store 0.8~1.2 wt.% H₂O upon different calibration methods, which agrees well with the water-rich mantle transition zone inferred from mineral viscosity (e.g., Fei et al., 2017) and the ringwoodite inclusion within the natural diamond crystal (Pearson et al., 2014). Therefore, by assuming the volume fraction of 60% wadsleyite/ringwoodite and 40% majoritic garnet, the transition zone from 410-660 km depth may store about twice of the total mass of oceanic water on the Earth's surface.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

We appreciate the help of H. Fischer for high-pressure cell assembly preparation, R. Njul for sample polishing, R. Huang and D. Krauß for EPMA analysis, and L. Wang for discussion. Comments from three anonymous reviewers are helpful to improve the manuscript. This work is funded by the Deutsche Forschungsgemeinschaft (DFG) to T. Katsura (KA3434/3-2, KA3434/7-1, KA3434/8-1, and KA3434/9-1, KA3434/11-1, KA3434/12-1).

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