In-situ infrared spectra of hydroxyl in wadsleyite and ringwoodite at high pressure and high temperature

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ABSTRACT

The infrared spectra of hydroxyl in synthetic hydrous wadsleyite (\(\beta\)-Mg\(_2\)SiO\(_4\)) and ringwoodite (\(\gamma\)-Mg\(_2\)SiO\(_4\)) were measured at room temperature up to \(\sim\)18.8 GPa for wadsleyite and up to \(\sim\)21.5 GPa for ringwoodite. High-temperature spectra were measured in an externally heated diamond anvil cell up to 650 °C at \(\sim\)14.2 GPa for wadsleyite and up to 900 °C at \(\sim\)18.4 GPa for ringwoodite. The synthetic samples reproduce nearly all the important OH bands previously observed at ambient conditions. Only subtle changes were observed in the infrared spectra of both minerals, both upon compression at room temperature and upon heating at high pressure. For wadsleyite, upon compression to \(\sim\)18.8 GPa, the frequencies of the bands at \(\sim\)3600 cm\(^{-1}\) remain almost unchanged, while the main bands at 3200-3400 cm\(^{-1}\) shift to lower frequencies. During heating at 14.2 GPa to 650 °C the bands at 3200-3400 cm\(^{-1}\) broaden and shift to slightly lower frequencies. For ringwoodite, upon compression to \(\sim\)21.5 GPa, the main bands at \(\sim\)3115 cm\(^{-1}\) progressively shift to lower frequencies. During heating at 18.4 GPa to 900 °C, no frequency shift was observed for the band at \(\sim\)3700 cm\(^{-1}\), but the band initially at \(\sim\)3115 cm\(^{-1}\) shifts very slightly to higher frequencies, which should yield almost the same band positions at \(\sim\)1300-1400 °C as those measured at ambient conditions. Our data suggest that water speciation in hydrous wadsleyite and ringwoodite at ambient conditions may be
comparable to that under mantle conditions, except perhaps for subtle changes in hydrogen bonding. The low OH-stretching frequencies in wadsleyite and ringwoodite under transition zone conditions imply a large H/D fractionation during degassing of the deep mantle. This may explain the apparent disequilibrium between the hydrogen isotopic composition of the upper mantle and the ocean.

KEY WORDS
Hydroxyl, wadsleyite, ringwoodite, infrared spectra, high-pressure & high-temperature, diamond anvil cell
INTRODUCTION

Wadsleyite ($\beta$-Mg$_2$SiO$_4$) and ringwoodite ($\gamma$-Mg$_2$SiO$_4$), the high pressure polymorphs of olivine ($\alpha$-Mg$_2$SiO$_4$), are the most abundant minerals in the transition zone of Earth’s mantle, between 410- and 660-km depth. Both minerals are able to accommodate up to several percent (by weight) of water as hydroxyl groups in their structure, and they likely constitute the most important water reservoir in Earth’s interior (e.g. Smyth 1987; Kohlstedt et al. 1996; Bolfan-Casanova et al. 2000). Water strongly affects many physical and chemical properties of wadsleyite and ringwoodite, including elastic moduli, seismic velocities, molar volume, rheological strength, thermal expansion, and electrical conductivity (Inoue et al. 1998; Kavner 2003; Smyth et al. 2003; Inoue et al. 2004; Jacobsen et al. 2004; Huang et al. 2005; Ye et al. 2009). The water contents in wadsleyite and ringwoodite can be high enough to shift phase boundaries between solid phases and to drastically reduce melting temperatures. As such, they may affect the structure of the transition zone, in particular the depth and width of the 410-km discontinuity and they may influence convection and dynamics of the whole mantle (Wood 1995; Bercovici and Karato 2003; Frost and Dolejs 2007; Richard and Bercovici 2009; Deon et al., 2013).

Structural models of the incorporation of H into wadsleyite and ringwoodite are indispensable for understanding water storage in the mantle and for predicting the effect of hydrogen on physical and chemical properties of the transition zone. Infrared spectroscopy is particularly useful for revealing the speciation of H in
minerals, and so far models of the dissolution of H in wadsleyite and ringwoodite have been derived mostly from infrared spectra (e.g. Bolfan-Casanova et al. 2000; Jacobsen et al. 2005; Deon et al., 2010; Panero et al. 2013). Neutron diffraction (Sano-Furukawa et al. 2011) and NMR studies (Stebbins et al. 2009; Griffin et al. 2013) have generally confirmed the structural models derived from infrared spectroscopy, although they have added a number of important details. Water dissolution in wadsleyite is generally well understood. The wadsleyite structure contains an Si$_2$O$_7$ group and one oxygen atom (O1) not attached to silicon. Smyth (1987) pointed out that this oxygen atom is electrostatically underbonded and should be a suitable site for protonation. In hydrous wadsleyite, protonation of O1 is charge compensated by Mg$^{2+}$ vacancies. The intense bands between 3300 and 3400 cm$^{-1}$ in the infrared spectrum of hydrous wadsleyite can be assigned to this substitution mechanism, with the OH vector pointing from the O1 atom to the O4 atom along a vacant M3 octahedral site. The weaker bands at ~3600 cm$^{-1}$ may be due to bent hydrogen bonds along the M3 edge, and the bands at ~3000 cm$^{-1}$ may be assigned to protonation of the tetrahedral edge of the Si$_2$O$_7$ group (Smyth 1987; Bolfan-Casanova et al. 2000; Jacobsen et al. 2005; Deon et al. 2010; Sano-Furukawa et al. 2011; Griffin et al. 2013). The high water solubility in ringwoodite is more difficult to understand, as ringwoodite has a spinel structure and spinels usually do not dissolve any measurable amount of water. The dissolution of water is probably mostly related to Mg$^{2+}$ vacancies on the octahedral sites, but substitution of Mg$^{2+}$ for Si$^{4+}$ on the tetrahedral site and perhaps silicon vacancies with a hydrogarnet type
defect may also be involved (Kudoh et al. 2000; Smyth et al. 2003; Mrosko et al., 2013). The infrared spectra of hydrous ringwoodite show a very broad band at ~3115 cm$^{-1}$ and some smaller bands at ~3695 and 2500 cm$^{-1}$. Possibly, the band at ~3695 cm$^{-1}$, which only appears at high water contents, is related to partial protonation of the octahedral edges, the band at 3115 cm$^{-1}$ is due to protonation on the edges of the tetrahedral sites, and the bands at 2500 cm$^{-1}$ are overtones of the in-plane X-OH bending modes or their combination with other vibrations (Bolfan-Casanova et al. 2000; Smyth et al. 2003; Chamorro Pérez et al. 2006). However, a number of other assignments of these bands have also been suggested; these include the assignment of the 3695 cm$^{-1}$ band to a hydrogarnet-type defect of four protons substituting for a Si vacancy (Blanchard et al. 2009; Mrosko et al. 2013) and the suggestion that the broad OH band at 3115 cm$^{-1}$ corresponds to the protonation of octahedral edges (Kudoh et al 2000; Blanchard et al. 2009). This uncertainty in the band assignment is mostly due to the cubic symmetry of ringwoodite, which precludes the observation of infrared pleochroism. Recent studies, based on annealing experiments (Mrosko et al. 2013) and low-temperature FTIR (Panero et al. 2013), suggest that the broad main band of ringwoodite at 3115 cm$^{-1}$ actually consists of several sub-bands involving different proton locations.

Up to now, models of hydrogen dissolution in wadsleyite and ringwoodite have been based exclusively on spectroscopic and diffraction data obtained at room temperature. Therefore, it is uncertain whether the available models correctly
describe the hydrogen substitution mechanisms deep in the mantle. Given the high
mobility of H, it is quite possible that its location may change upon quenching of a
sample from high temperature and pressure. In particular, the very broad main band
of ringwoodite could be due to some proton disordering during quenching. In order
to provide additional insights into the true hydrogen speciation in wadsleyite and
ringwoodite at mantle conditions, we present here in-situ FTIR spectra of hydrous
wadsleyite and ringwoodite at simultaneous high-pressure and high-temperature
conditions.

## EXPERIMENTAL METHODS

The starting material for the synthesis of hydrous Mg$_2$SiO$_4$ wadsleyite and
ringwoodite were two high-purity synthetic single crystals of forsterite (diameter, 1.0
mm; length, 1.0 mm). A mixture of talc plus brucite powder with a weight ratio of
1.4:1 was added as water source (corresponding to several percent H$_2$O relative to
the entire charge). For each experiment, the starting materials were sealed in a
welded Pt capsule (outer diameter, 1.6 mm; inner diameter, 1.3 mm; length, ~3 mm).
The syntheses were carried out in a 1200-tonne multi anvil apparatus at 18 GPa and
1400 °C for wadsleyite and at 22 GPa and 1400 °C for ringwoodite, using a 10/5 and
10/4 octahedral assembly (octahedron length/truncation length) and a lanthanum
chromate heater. The run duration was 200 min. Temperature was monitored and
controlled to within ±1 °C during the experiments using a W3%Re/W25%Re
thermocouple. At the end of the experiment, the sample was quenched to room
temperature within several seconds by switching off the power to the heating circuit. The recovered crystals were of high quality, free of any visible impurities or inclusions and up to ~300 μm in size. Water contents of the synthesized samples were determined by unpolarized infrared analysis on doubly-polished thin sections (~30 μm thick) at ambient conditions. The spectra were integrated from 2300 to 3800 cm\(^{-1}\) and water contents were determined using the mineral-specific extinction coefficients of 73000 L/(mol·cm\(^2\)) for wadsleyite by Deon et al. (2010) and of 100000 L/(mol·cm\(^2\)) for ringwoodite by Koch-Müller and Rhede (2010). The estimated water content is ~1.5% H\(_2\)O for the wadsleyite and ~1.1% H\(_2\)O for the ringwoodite.

Hydrostatic high-pressure and high-temperature conditions were generated in a symmetric piston-cylinder-type diamond anvil cell (DAC) with diamonds of 300 μm culet size and an external resistive heater. Prior to sample loading, a piece of Re foil (~200 μm thickness and ~0.4 × 0.4 cm length × width) was pre-indent in the cell to a thickness of ~40 μm. A 150-μm-diameter hole was then drilled into the gasket. A ~15 μm thick thin section of the sample, with length and width of about 40 and 50 μm, was loaded into the sample chamber between two diamond anvils together with a <8-μm-diameter ruby sphere for pressure calibration. The sample chamber was then filled with Ne gas as pressure transmitting medium at ~0.15 GPa using a high-pressure gas-loading apparatus developed at the Bayerisches Geoinstitut. The cell was sealed at 1-2 GPa. Two loadings were prepared for each mineral: one for
compression to high pressure at room temperature and the other one for heating to high temperature at constant pressure (~14.2 GPa for wadsleyite and ~18.4 GPa for ringwoodite). In the high temperature runs, the resistive heater was placed inside the DAC and around the gasket between the diamond anvils (in air), and an S-type thermocouple (Pt-Pt$_{90}$Rh$_{10}$), located very close to the gasket hole (~200 $\mu$m distance), was used to estimate temperature. The pressure prior to and after each infrared analysis was determined by ruby fluorescence with a Jobin Yvon Labram spectrometer as calibrated for hydrostatic conditions by Mao et al. (1986) and Rekhi et al. (1999). For each measurement, the variation of pressure was <0.2 GPa, usually <0.1 GPa, and the variation of temperature was <1 °C as recorded by the S-type thermocouple.

For the experiments at room temperature, infrared spectra were recorded using a Bruker IFS 120 spectrometer coupled to a Bruker IR microscope (IRscope I); while for the experiments at high temperature, infrared spectra were obtained using a Bruker IFS 125 spectrometer with the same microscope. For each measurement, 70 to 200 scans were acquired with 4 cm$^{-1}$ resolution using a tungsten light source, a Si-coated CaF$_2$ beam splitter and a narrow-band MCT detector. During the measurements, the spectrometer was evacuated and the optics of the microscope was continuously purged with H$_2$O- and CO$_2$-free, purified air. The background spectra were measured through the diamonds inside the Ne-filled gasket holes. The band positions of each spectrum were obtained by deconvoluting the spectra into Gaussian
components using the Peakfit program (Ver. 4.12, Systat Software Inc.). Interference fringes in the spectra, due to multiple reflections between a sample and diamond surfaces, were removed either by the method developed by Neri et al. (1987) or were deconvoluted with the Peakfit software together with the OH bands of the sample. Recovered samples were examined by Raman spectroscopy; no irreversible phase changes were found.

RESULTS AND DISCUSSION

Spectra at ambient conditions

Infrared spectra of the synthesized hydrous wadsleyite and ringwoodite collected at ambient conditions, at high pressures (room temperature) and at high temperatures (with pressure maintained at ~14.2 GPa for wadsleyite and ~18.4 GPa for ringwoodite) are illustrated in Fig. 1 and 2, together with spectra of the samples at ambient conditions after the experiments. At ambient conditions, the samples show the typical OH-related absorption bands in the 2300-3800 cm\(^{-1}\) range previously reported for the corresponding mineral. For wadsleyite, the spectrum shows bands at ~3660, 3582, 3360 and 3320 cm\(^{-1}\), similar to those reported by Bolfan-Casanova et al. (2000), Jacobsen et al. (2005) and Deon et al. (2010), but the weak absorption centered at ~3000 cm\(^{-1}\) observed in some studies is not obvious in our sample (Fig. 1a). For ringwoodite, the spectrum contains a broad and strong band at ~3115 cm\(^{-1}\), a weaker band at ~3695 cm\(^{-1}\), and one weak doublet at ~2500 cm\(^{-1}\) (with two bands at ~2550 and 2472 cm\(^{-1}\), respectively). Similar to observations in previous studies
Behavior of wadsleyite upon compression and heating

Upon compression of wadsleyite to ~18.8 GPa (Fig. 1a and 3a), the two bands at ~3660 and 3582 cm\(^{-1}\) remain almost unchanged, while the bands at 3360 and 3320 cm\(^{-1}\) progressively shift to lower frequencies. The general trends of the band positions with increasing pressure are similar to those previously observed by Raman spectroscopy (Kleppe et al., 2001) and by FTIR (Deon et al., 2010) for hydrous wadsleyite (\(\beta\)-Mg\(_2\)SiO\(_4\)) with different water contents (~1.6% H\(_2\)O in the former and 0.8% H\(_2\)O in the latter study). The frequency shift for the bands initially at 3360 and 3320 cm\(^{-1}\) is best described by by second-order polynomial fits with first and second order pressure derivatives of -9.80 cm\(^{-1}/\)GPa and 0.13 cm\(^{2}/\)GPa\(^2\) for the band at 3360 cm\(^{-1}\) and of -10.18 cm\(^{-1}/\)GPa and 0.09 cm\(^{1}/\)GPa\(^2\) for the band at 3320 cm\(^{-1}\). The difference to the linear fits given by Kleppe et al. (2001) and Deon et al. (2010) may be due to a different deconvolution of the bands. For example, in Deon et al. (2010), the main broad band was resolved into three components in contrast to the two bands in the present study; while in Kleppe et al. (2001), the resolution of
the Raman spectra was not sufficient for further deconvolution.

High-temperature spectra of wadsleyite at 14.2 GPa up to 650 °C are shown in Figure 1b. The positions of the two bands at ~3660 and 3582 cm⁻¹ do not seem to change much, although the appearance of relatively strong interference fringes in the spectra makes it difficult to precisely locate these bands. Not that the intensity of these interference fringes is very sensitive to the degree of parallelity of sample surfaces and to the beam path through the diamond cell, so that major changes may occur for different experiments, even for samples from the same charge. The bands initially at 3320 cm⁻¹ and at 3360 cm⁻¹ at ambient conditions cannot be well resolved from each other anymore, but the envelope of the two bands appears to shift slightly to lower frequencies with the temperature derivative of 0.03 cm⁻¹/°C (Fig. 3b).

Behavior of ringwoodite upon compression and heating

High-pressure spectra of ringwoodite are shown in Figure 2a. Unfortunately, the occurrence of interference fringes makes it difficult to locate the weaker bands, but the main band at 3115 cm⁻¹ gradually shifts to lower frequencies. A similar behavior of hydrous ringwoodite under pressure was observed by Chamorro Pérez et al. (2006) and by Koch-Müller et al. (2011). The shift of the band initially at ~3115 cm⁻¹ may be described by a second order polynomial fit, which gives first and second order pressure derivatives of -12.3 cm⁻¹/GPa and 0.23 cm⁻¹/GPa², agreeing well with the reported -12.1 cm⁻¹/GPa and 0.20 cm⁻¹/GPa² by Chamorro Pérez et al. (2006).
Upon heating the ringwoodite to 900 °C at ~18.4 GPa, no frequency shift was observed for the band at ~3695 cm\(^{-1}\), but the band at ~2970 cm\(^{-1}\), initially at ~3115 cm\(^{-1}\) at ambient conditions, shifts very slowly to higher frequencies (Fig. 2b and 4b). The band initially located at ~2970 cm\(^{-1}\) can be best fitted by a linear function, with the temperature derivative of 0.10 cm\(^{-1}\)/°C. A closer inspection of the spectra reveals that at 18.4 GPa and 27 °C, a shoulder is visible at the high-frequency side of the main absorption peak. Deconvolution of the spectra suggests that this shoulder is due to a Gaussian component at ~3367 cm\(^{-1}\). This agrees well with a separate component in the ringwoodite spectrum detected by low-temperature FTIR spectroscopy (Panero et al. 2013). At higher temperatures, this shoulder becomes less prominent; however, deconvolution of the spectrum measured at 900 °C suggests that it is still present, although perhaps with somewhat reduced intensity (Fig. 5).

**Implications for water storage in the transition zone**

Temperatures in the transition zone of Earth’s mantle, where wadsleyite and ringwoodite are stable, are expected to be in the range of 1400 to 1600 °C (Ito and Katsura 1989). Unfortunately, with present technology it is not possible to do infrared spectroscopy in-situ under these conditions; the 900 °C reached in our measurements with ringwoodite are already close to the upper temperature limit of externally heated diamond anvil cells. Directly probing the speciation of hydrogen in minerals under transition zone conditions would likely require the use of a different technology, such as high-pressure neutron diffraction. However, the data presented
here are at least consistent with the hypothesis that water speciation in wadsleyite and ringwoodite under transition zone conditions is not fundamentally different from that inferred from studies at ambient conditions.

A particularly important result of our study is that the strength of hydrogen bonding in wadsleyite and ringwoodite under transition zone conditions may be similar to that under ambient conditions. In particular for ringwoodite, the effects of increasing pressure and increasing temperature on the OH stretching frequency nearly cancel out. It has been shown by Dobson et al. (1989) that, based on the measured H/D fractionation factors of 12 minerals (pectolite, diaspor, zoisite, boehmite, epidote, muscovite, kaolinite, biotite, hornblende, annite, phlogopite and chrysotile) and of two glasses (rhyolitic obsidian and albite-orthoclase glass), a very good negative correlation exists between the OH stretching frequency in a mineral and the H/D isotopic fractionation factor between the mineral and water vapor (Fig. 6). Such a correlation of hydrogen bond strength with the fractionation factor is theoretically expected, and has been partly confirmed for mantle samples by Bell and Ihinger (2000). They observed that nominally anhydrous mantle augite, orthopyroxene and garnet, characterized by lower OH stretching frequency (3560-3460 cm$^{-1}$) relative to phlogopite (3660-3710 cm$^{-1}$), generally have lower $\delta D$ (-90‰ to -110‰) than phlogopite (typically $\delta D = -80‰$). Moreover, the results of Dobson et al. (1989) demonstrate that the H/D fractionation curves as a function of temperature are usually parallel between different minerals, indicating that the relative fractionation
between the mineral pairs would be much less affected by temperature than the
tractionation between the minerals and water vapor. The stretching frequencies in
wadsleyite and particularly in ringwoodite are very low compared to most other
hydrous minerals, such as serpentine, amphibole and micas. This would imply that
H/D fractionation between wadsleyite and particularly ringwoodite and water vapor
should be much stronger than for the minerals formed by water-rock interaction on
the ocean floor. For example, the predicted fractionation factor of ringwoodite is
\( \sim 90\% \) at 18.4 GPa and 400 °C (Fig. 6). Possibly, this could provide an explanation
for the large difference in hydrogen isotopic composition between seawater (\( \delta D =
0\% \)) and the upper mantle (\( \delta D = -80\% \)), which is difficult to explain by equilibrium
between these two reservoirs (Shaw et al. 2008 and references therein). As
wadsleyite and ringwoodite are the main reservoirs of water in the mantle (e.g.
Bolfan-Casanova et al. 2000) and as the oceans likely formed by degassing of
Earth’s interior, the isotopic composition of the ocean may reflect equilibrium
isotope fractionation between a hydrous fluid and wadsleyite or ringwoodite. The
low OH stretching frequency of these minerals would suggest that this process
should lead to a strong depletion of deuterium in the solid residue. The present,
strongly deuterium-depleted hydrogen isotope composition of the upper mantle may
then be inherited from this initial transition zone signature by mantle mixing and
upwelling.

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Figure captions

Fig. 1  In situ infrared spectra of wadsleyite (a) to ~18.8 GPa at room temperature, and (b) to 650 °C at ~14.2 GPa. The spectra were normalized to 1 mm thickness and vertically offset. The spectrum in (a), labeled as after decompression, was measured from the sample after final decompression. The grey spectra in (b), labeled as 400, 200 and 25 °C, respectively, were measured during cooling, and the dashed spectrum in (b), labeled as Room-P & T, was measured at ambient conditions, as was the one labeled as 1 bar in (a). The variation of pressure before and after each measurement was usually less than 0.1 GPa for (a) and less than 0.2 GPa for (b). All the spectra were measured within the DAC.

Fig. 2  In situ infrared spectra of ringwoodite (a) to ~21.5 GPa at room temperature, and (b) to 900 °C at ~18.4 GPa. The spectra were normalized to 1 mm thickness and vertically offset. The spectrum in (a), labeled as after decompression, was measured from the sample after final decompression (note that the crystal cracked during the final rapid decompression). The grey spectra in (b), labeled as 200, 100 and 27 °C, respectively, were measured during cooling, and the dashed spectrum in (b), labeled as Room-P & T, was measured at ambient conditions, as was the one labeled as 1 bar in (a). The variation of pressure before and after each measurement was usually less than 0.1 GPa for (a) and less than 0.2 GPa for (b). All the spectra were measured within the DAC.

Fig. 3  Frequencies of OH bands in wadsleyite as a function of (a) pressure (room temperature), and (b) temperature (~14.2 GPa). Only the most prominent bands are
shown. The uncertainty in the frequencies is usually smaller than the symbol size. The curved lines are from second-order polynomial fits: in (a), band initially at

\[ \nu = 3361(\pm 2) - 9.80(\pm 0.68) \times P + 0.13(\pm 0.03) \times P^2, \]

band initially at

\[ \nu = 3324(\pm 2) - 10.18(\pm 0.53) \times P + 0.09(\pm 0.02) \times P^2; \]

in (b), band at

\[ \nu = 3223(\pm 2) + 0.03(\pm 0.01) \times T - 1.43 \times 10^{-4} (\pm 0.21 \times 10^{-4}) \times T^2, \]

where \( \nu \) is frequency (cm\(^{-1}\)), \( P \) is pressure (GPa) and \( T \) is temperature (°C).

Fig. 4  Frequencies of OH bands in ringwoodite as a function of (a) pressure (room temperature), and (b) temperature (~18.4 GPa). Only the most prominent bands are shown. The uncertainty in the frequencies is usually smaller than the symbol size.

For the band initially at ~3115 cm\(^{-1}\), the curved line in (a) is from a second-order polynomial fit:

\[ \nu = 3116(\pm 2) - 12.3(\pm 0.6) \times P + 0.23(\pm 0.03) \times P^2; \]

and the line in (b) is from a linear fit:

\[ \nu = 2952(\pm 3) + 0.10 (\pm 0.01) \times T, \]

where \( \nu \) is frequency (cm\(^{-1}\)), \( P \) is pressure (GPa) and \( T \) is temperature (°C).

Fig. 5. Deconvolution of the FTIR spectra of ringwoodite at 18.4 GPa: (a) at 27 °C and (b) at 900 °C. The spectra were deconvoluted by the Peakfit software (\( r^2 > 0.99 \) for the fitting). The resolved shoulder component is ~3367 cm\(^{-1}\) at 27 °C (see text).

The bands at ~2500 cm\(^{-1}\) cannot be reasonably resolved due to interference (Fig. 2b), and the added components here were only for fitting.

Fig. 6  Fractionation factor (1000 ln \( \alpha_{\text{vapor-mineral}} \)) of H between minerals and water vapor at 400 °C (modified after Dobson et al. (1989) and Bell and Ihinger (2000)). The average OH frequency of ringwoodite (vertical thick line) at 18.4 GPa and 400 °C is ~3000 cm\(^{-1}\) according to our results, yielding a fractionation factor of
440 \sim 90\%.$
Figure 1

Wave number (cm$^{-1}$)

Absorbance

After decompression

1 bar
0.8 GPa
1.9 GPa
3.0 GPa
4.4 GPa
6.2 GPa
8.2 GPa
9.9 GPa
11.3 GPa
13.2 GPa
15.0 GPa
17.2 GPa
18.8 GPa

Room-P = 8.1 GPa
14.2 GPa
25°C

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Fig. 3

Open symbols: increasing pressure
Solid symbols: decreasing pressure

(b) Open symbols: heating
Solid symbols: cooling
Open symbols: increasing pressure
Solid symbols: decreasing pressure

(a)

Open symbols: heating
Solid symbols: cooling

(b)

Fig. 4
Fig. 6

H-isotopic fractionation at 400 °C

- minerals in Dobson et al. (1989)
- glasses in Dobson et al. (1989)

Bell and Ihinger (2000)

1000 ln α_vapor-mineral

Wavenumber (cm^{-1})

0  2000  3000  3200  3400  3600  3800  4000

80  60  40  20  0