Effect of iron on the compressibility of hydrous ringwoodite

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ABSTRACT

Single crystals of hydrous ferroan ringwoodites with compositions $(Mg_{0.97}Fe_{1.00})_{1.97}Si_{0.98}H_{0.13}O_4$ and $(Mg_{1.21}Fe_{0.66}^{3+}Fe_{1.00})_{1.97}Si_{0.97}H_{0.06}O_4$ have been synthesized. Their lattice parameters at ambient conditions are a = 8.1597(6) Å and V = 543.28(13) Å³ and a = 8.1384(3) Å and V = 539.03(7) Å³, respectively. The unit-cell lattice parameters were measured at different pressures up to about 9 GPa by means of X-ray single-crystal diffraction. The *P*-*V* data were fitted with a second-order Birch-Murnaghan equation of state (*K'* fixed to the value of 4) refining to the following equation of state parameters: $V_0 = 543.32(7)$ Å³ and $K_{T0} = 186.5(9)$ GPa for $(Mg_{0.97}Fe_{1.00})_{1.97}Si_{0.98}H_{0.13}O_4$ and $V_0 = 539.01(5)$ Å³ and $K_{T0} = 184.1(7)$ GPa for $(Mg_{1.21}Fe_{0.66}^{2+}Fe_{0.1}^{3+})_{1.97}Si_{0.97}H_{0.06}O_4$. Structural refinements indicate the presence of significant octahedral vacancies in sample $(Mg_{1.21}Fe_{0.66}^{2+}Fe_{0.1}^{3+})_{1.97}Si_{0.97}H_{0.06}O_4$ due to the oxidation of 0.1 apfu of ferric iron. Correlation between the O-O distances of the octahedral edges and the shift of the OH-stretching frequency suggest that the H incorporation occurs at the octahedral site.

Keywords: Compressibility, hydrous ringwoodite, single crystal, IR spectrum

INTRODUCTION

Ringwoodite (Mg,Fe)₂SiO₄, a high-pressure polymorph of olivine, is thought to be the most abundant mineral in the lower part of the Earth's transition zone (510 km depth) as well as in the deep part of the martian mantle at 1200 km depth. It possesses the cubic normal spinel structure with the space group $Fd\overline{3}m$. The O atoms are arranged in a cubic close packing with silicon occupying the tetrahedral interstitial sites and magnesium and iron the octahedral interstitial sites, respectively. Kohlstedt et al. (1996) evidenced that nominally anhydrous minerals such as Mg₉₀-ringwoodite are able to accommodate up to 2.4 wt% H₂O in the form of OH-groups in their structure, which implies a potentially enormous water reservoir in the Earth's mantle. Since physical properties such as compressibility of ringwoodite determine the characteristics (e.g., seismic velocities) of the lower part of the mantle transition zone, dry and hydrous Mg₂SiO₄ ringwoodites have been studied intensively using different techniques such as Brillouin spectroscopy, ultrasonic interferometry, and X-ray diffraction (Hazen 1993; Inoue et al. 1998; Yusa et al. 2000; Jackson et al. 2000; Li 2003; Sinogeikin et al. 2003; Wang et al. 2003; Jacobsen et al. 2004; Manghnani et al. 2005; Jacobsen and Smyth 2006). Jackson et al. (2000) and Li (2003) determined an isothermal bulk modulus of K_{T0} of 185 GPa for dry Mg-ringwoodite using Brillouin spectroscopy and ultrasonic interferometry. Dry iron-bearing ringwoodite with up to 10 mol% iron appears to have a slightly higher bulk modulus $[K_{T0} = 188(3) \text{ GPa}]$ than the pure Mg-end-member (Sinogeikin et al. 2003), although the difference is negligible, given the uncertainties. Anhydrous pure iron-end-member ringwoodite

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measured in diamond anvil cells (DAC) shows a distinctly higher bulk modulus of 207(3) GPa (Hazen 1993). In contrast, hydrous Mg-ringwoodites with 2.3 wt% H₂O have a smaller isothermal bulk modulus with K_{T0} ranging between 155(4) and 165.8(5) GPa (Inoue et al. 1998; Wang et al. 2003). Powder X-ray diffraction data of hydrous Mg-ringwoodite with 2.8 wt% H2O also resulted in a significantly smaller bulk modulus of 148(1) GPa (Yusa et al. 2000). A theoretical study by Li et al. (2009) also predicts linear decrease of bulk modulus of ringwoodite with increasing water content. Isothermal bulk modulus of hydrous ferroan ringwoodite (~1 wt% H₂O; 11 atom% iron) was determined using ultrasonic interferometry as well as powder X-ray diffraction and ranges from 175(3) to 177(4) GPa (Jacobsen et al. 2004; Manghnani et al. 2005; Jacobsen and Smyth 2006). Water and iron substitution into the ringwoodite structure appears, therefore, to have an opposite effect on its compressibility. To better constrain this behavior, we have performed a single-crystal X-ray diffraction compressibility study at room temperature using well-characterized, iron-rich hydrous ringwoodite samples. Knowledge of the effect of iron on the compressibility of ringwoodite is particularly important for the interpretation of the structure of iron-rich planetary mantles such as those of Mercury and Mars.

EXPERIMENTAL METHODS

Sample characterization

Samples of hydrous ferroan ringwoodite were synthesized from a stoichiometric MgFeSiO₄+9.5 wt% H₂O starting mixture [Fe₂SiO₄+Mg(OH)₂+SiO₂] at 15 GPa and 1150 °C (run 3854) as well as at 20.5 GPa and 1400 °C (run 4218) using a 1200 ton multi-anvil press. The starting material was loaded into welded Pt-capsules with 1.6 and 1.2 mm diameter for 14/8 and 10/4 multi-anvil assemblies, respectively. Heating duration was 30 min for run 3854 and 3.5 h for run 4218. Ringwoodite was the only phase present in the synthesis product of run 3854, whereas it was the dominant

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phase coexisting with stishovite and magnesiowüstite in run 4218.

Chemical composition was measured on the polished surface of several crystals mounted in epoxy-resin using a JEOL JXA-8200 microprobe at Bayerisches Geoinstitut. Chemical analyses were performed using wavelength dispersive spectroscopy at 15 kV and 20 nA for several point analyses on different crystals. Standards used for calibration were hematite (Fe₂O₃) for Fe and diopside (CaMgSi₂O₆) for Mg and Si. Raw intensities were corrected by ZAF matrix-correction and converted into oxide weight percent. Results of the chemical analyses are given in Table 1.

To determine the amount of Fe³⁺ present in the run products, ringwoodite crystals (runs 3854 and 4218) were crushed to powder and placed in a suspension with ethanol on a holey 100 mesh copper grid covered with a carbon film. Selected area electron diffraction (SAED) and electron energy-loss spectroscopy (EELS) were performed on a Philips CM20 FEG transmission electron microscope operating at 200 kV. Electron energy-loss near-edge structure (ELNES) spectra were collected using energy-loss spectrometer (Gatan PEELS 666). Quantification of Fe³⁺/ Σ Fe ratio was done following the procedure described by Van Aken et al. (1998) and Frost et al. (2001). Integration of the two peaks of the iron L_3 and L_2 ionization edge in the spectra yields a Fe³⁺/ Σ Fe = 0.01(5) ratio (run 3854) and a Fe³⁺/ Σ Fe = 0.13(5) ratio (run 4218).

Water concentration of hydrous ringwoodite was determined by Fourier transformed infrared spectroscopy (FTIR). The BRUKER IFS 120 high-resolution FTIR spectrometer with IR microscope is equipped with a tungsten source and Si-coated CaF₂ beam splitter for water concentration analyses. The double-sided polished single crystals (~30 µm thickness) recovered from the high-pressure study were placed on a CaF₂ plate during unpolarized FTIR measurements. Optically clear areas of the single crystal were analyzed using a spot size of 60 µm limited by the objective aperture. The IR spectral region between 2000 and 3800 cm⁻¹ has been attributed to the O-H stretching modes (Kohlstedt et al. 1996; Bolfan-Casanova et al. 2000) and the procedure described by these authors have been used for calculating the water content of our samples. Quantification of water concentration was done after the calibration of Paterson (1982) applying the formula to the obtained spectra (Eq. 1)

$$C_{\rm OH} = \frac{X_i}{150\zeta} \int \frac{K(\overline{\nu})}{(3780 - \overline{\nu})} d\overline{\nu} \, .$$

The concentration of OH is given in ppm weight (ppm wt); the density factor X_i is 2141 for (Mg,Fe)₂SiO₄; ζ is the orientation factor, which is 1/3 for unpolarized measurements; K(v) is the absorption coefficient (cm⁻¹) for a given wavenumber v. Correlation of OH-stretching frequency and absorption coefficient for ringwoodite are empirical such that water contents are estimates with an uncertainty of 30–50% (Kohlstedt et al. 1996). Obtained spectra were corrected for thickness and the region from 2000–3730 cm⁻¹ was integrated using the calibration of Paterson (1982) to estimate the H₂O content in wt% (Table 1). The resulting formulae of hydrous ringwoodites are as follows: (Mg_{0.97}Fe_{1.00})_{1.97}Si_{0.98}H_{0.14}O₄ (run 3854) corresponding to 7088 ppm wt H₂O and (Mg_{1.21}Fe³_{0.66}Fe⁴_{0.11})_{1.97}Si_{0.97}H_{0.06}O₄ (run 4218) corresponding to 3746 ppm wt H₂O.

 TABLE 1.
 Chemical compositions of ringwoodite based on electron microprobe analyses, electron energy-loss, and IR spectroscopy (standard deviations are given in parentheses)

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Oxides (wt%)*	Run 3854	Run 4218							
SiO ₂	35.2(2)	36.0(2)							
MgO	23.3(2)	30.2(3)							
FeO	42.8(3)	29.4(4)							
Fe ₂ O ₃ †	-	4.9(1)							
H ₂ O‡	0.71	0.37							
sum	102.0(4)	100.9(3)							
Cations based on 4 O atoms									
Si	0.98	0.97							
Mg	0.97	1.21							
Fe ²⁺	1.00	0.66							
Fe ³⁺ †	-	0.10							
H‡	0.13	0.07							
sum	3.08	3.01							
Mg/(Mg+Fe)	0.49	0.62							
Water c	ontent based on IR spectra								
Main peak maximum	3250 cm ⁻¹	3300 cm ⁻¹							
H₂O (ppm wt)	7088	3746							
* Average of 30 (4218) and 5	5 (3854) microprobe measure	ments.							
† From EELS analyses.	•								
/									

[‡] From IR spectroscopy measurements.

X-ray single-crystal diffraction at room pressure

Two single crystals, one for each run product, were selected for the high-pressure X-ray diffraction experiments. Previous to the measurements in the diamond anvil cell, intensity data were collected at ambient conditions using an Xcalibur diffractometer with MoK a radiation operated at 50 kV and 40 mA, equipped with a CCD detector and a graphite monochromator with the single crystals mounted on a glass fiber. Combined omega and phi scans were chosen to obtain a coverage of half reciprocal sphere up to 20 max = 80° for sample 4218 and up to 20 max = 90° for sample 3854. The exposure time was 15 s/frame. Lorentz and polarization factors as well as an analytical absorption correction based on the crystal shape were taken into account for the correction of the reflection intensities using the CrysAlis package (Oxford Diffraction 2006).

Structure refinements were performed based on F² using the SHELX97 program package (Sheldrick 1997) in the WinGX 1.70.01 system (Farrugia 1999) with space group $Fd\overline{3}m$ and anisotropic displacement parameters, following a similar procedure as described by Smyth et al. (2003). Fully ionized scattering curves (Ibers and Hamilton 1974) were used for all cations. Since the cation occupancies of light elements like Si and Mg depend on the scattering curve used for oxygen, the distributed scattering factor of the oxygen atom between the atomic scattering curve and the scattering curve of O2- (Tokonami 1965) was refined together with the cation occupancies at the initial state of the refinements. This procedure resulted in a similar scattering distribution for both samples of 50% O and 50% O2-. This value was then fixed during the last cycles of refinements. The iron content from the microprobe analysis was constrained to be at the octahedral site. Magnesium and Si occupancies were refined at the octahedral and at the tetrahedral sites, respectively, without any constraint. Unit-cell parameters, data collection and refinement details. fractional atomic coordinates, equivalent thermal parameters, and polyhedral bond lengths obtained in this study are reported in Table 2.

High-pressure experiments

The two ringwoodite single crystals studied at room conditions have the following dimensions: $120 \times 100 \times 30 \,\mu\text{m}$ (sample 3854) and $100 \times 50 \times 30 \,\mu\text{m}$ (sample 4218). They were loaded into two diamond anvil cells (DAC) with diamond culets of 600 μm in diameter. Steel gaskets preindented to 90 μm hickness with 250 μm holes and a 4:1 mixture of methanol:ethanol as pressure-transmitting medium were used. Ruby crystals were also loaded into the DACs for pressure determination during the high-pressure experiments (Mao et al. 1986). Unit-cell parameters were measured as a function of pressure with a Huber four-circle single-crystal diffractometer at the Bayerisches Geoinstitut. Peak positions were determined using the eight-position centering method (King and Finger 1979) to minimize experimental aberrations. Unit-cell parameters measured up to ~9 GPa were obtained using vector-least-square refinements (Ralph and Finger 1982). The unit-cell parameters of the hydrous ferroan ringwoodites at different pressures are given in Table 3.

RESULTS

Crystal-chemistry of hydrous Fe-bearing ringwoodite

The unit-cell volume of ringwoodite increases with increasing Fe content (Fig. 1). There is some evidence that water substitution also increases the unit-cell volume of ringwoodite (Smyth et al. 2003) as suggested by the fit of the hydrated samples, which all lie above the linear trend between the anhydrous end-members (dotted and solid lines, respectively depicted in Fig. 1). Octahedral, M-O, and tetrahedral, T-O, bond distances obtained from the structural refinements of our samples are compared with those reported in the literature for ringwoodites having different Mg/(Mg+Fe) ratios and water contents (Figs. 2a and 2b). The M-O bond distance increases with increasing Fe content of ringwoodite (Fig. 2a), whereas the T-O bond distance slightly decreases with increasing Fe content (Fig. 2b).

Fe-substitution also has a strong effect on the OH-stretching mode of hydrous ringwoodite. Unpolarized infrared spectra of our two samples (Fig. 3) show broad OH-absorption bands with the most intense absorption peaks centered at about 3250 and 3300 cm⁻¹ for samples 3854 and 4218, respectively. These bands

Pressure (GPa)

Sample	Run 3854	Run 4218		
N _{meas}	15250	12420		
Nunique	136	104		
N _{obs}	111	76		
R _{int}	0.0299	0.0476		
R	0.0291	0.0391		
$R_{\rm w} (F > 4\sigma)$	0.0200	0.0212		
wR2	0.0565	0.0602		
GooF	1.019	0.862		
No. parameters	10	10		
a (Å)	8.1597 (6)	8.1384 (3)		
V (Å ³)	543.28 (13)	539.07 (7)		
	Octahedral site			
Mg occ	0.496 (2)	0.540 (3)		
Fe occ	0.495 (1)	0.381 (1)		
Total occupancy	0.991	0.921		
U ₁₁	0.00649 (15)	0.0073 (3)		
U ₁₂	-0.00016 (10)	-0.0004 (2)		
U _{eq}	0.00649 (15)	0.0073 (3)		
M-O (Å)	2.1045 (9)	2.0972 (14)		
O-M-O (°)	86.64 (4)	86.73 (7)		
O-M-O (°)	93.36 (4)	93.27 (7)		
O-O (non-shared)	2.888 (2)	2.880 (4)		
O-O (shared)	(shared) 3.062 (2)			
	Tetrahedral site			
Si occ	1.0007 (4)	0.9904 (7)		
$U_{11} (= U_{eq})$	0.0064 (3)	0.0080 (4)		
Si-O (Å)	1.6580 (15)	1.657 (2)		
0-0 (Å)	2.708 (2)	2.705 (4)		
	O atom site			
x	0.24231 (11)	0.24253 (16)		
U_{11}	0.0070 (3)	0.0084 (6)		
U ₁₂	-0.0001 (2)	0.0011 (5)		
Um	0.0070 (3)	0.0084 (6)		

TABLE 2. Structure refinement data for the two ringwoodite samples of this study

TABLE 3. Unit-cell parameter measured as a function of pressure

a (Å) Run 4218 0.000(6) 8.1384(3) 539.03(7) 0.64(1) 8.1286(4) 537.10(8) 1.08(5) 8.1217(3) 535.73(7) 1.63(2) 534.40(6) 8.1150(3) 532.70(7) 2.23(1)8.1064(3) 2.99(0) 8.0957(3) 530.61(6) 3.64(2) 8.0872(3) 528.93(6) 4.07(3)* 8.0806(4) 527.63(7) 5.05(4)* 8.0674(5) 525.05(10) 5.68(0) 8.0597(3) 523.55(7) 6.44(4)8.0505(5) 521.76(9) 7.21(3) 8.0460(4) 519.83(9) 7.83(3) 8.0328(4) 518.32(7) 8.27(0) 8.0269(3) 517.19(6) 8.54(1) 8.0235(3) 516.52(6) 871(2) 8 0211(4) 516 07(8) 8.90(3) 8.0188(3) 515.61(6) Run 3854 0.0001(1) 543.28(13) 8.1597(6) 0.99(1) 8.1455(3) 540.45(6) 1.44(3)8.1388(3) 539.11(6) 2.20(2) 8 1 2 9 0 (3) 537.17(7) 2.71(1) 8.1218(4) 535.75(8) 3.30(4) 8.1141(3) 534.23(7) 3.81(1) 8.1068(3) 532.79(6) 4.42(1) 8.0988(4) 531.20(8) 5.50(0)8.0845(3) 528.40(6) 6 38(0) 8 0732(4) 526 19(7) 6.93(0) 8.0662(3) 524.82(7) 7.31(4) 8.0609(3) 523.79(7) 7.96(1) 8.0532(3) 522.28(6) 8.27(1) 8.0495(3) 521.57(7) 8.0494(4) 521.54(8) 8.31(2)3 8.48(2) 8 0467(3) 521.02(6) 8.77(2) 8.0438(3) 520.47(6) * Data points measured during decompression.

Note: U_{eq} represent the isotropic equivalent of the anisotropic temperature factors; N denotes number of reflections.



FIGURE 1. Unit-cell volume of anhydrous and hydrous ringwoodite as a function of magnesium content; solid symbols = hydrous ringwoodite [Kudoh et al. (2000), 2 wt% H₂O; Smyth et al. (2003), 0.74 wt% H₂O Fo100-ringwoodite, 0.86 wt% H2O Fo90-ringwoodite, 1.07 wt% H2O Fo87ringwoodite]; open symbols = anhydrous ringwoodite; solid line = linear fit of anhydrous samples, dotted line = linear fit of hydrous samples

are clearly much broader than the O-H absorption bands reported for the pure hydrous Mg₂SiO₄ ringwoodite (Bolfan-Casanova et al. 2000; Smyth et al. 2003). Two weak absorption bands have also been observed in the IR spectra of pure hydrous Mg₂SiO₄ ringwoodite at lower (~2450 cm⁻¹) and higher (~3700 cm⁻¹) wavenumbers and have also been assigned to O-H stretching vibrations (Bolfan-Casanova et al. 2000), although there is some suggestion that the lower energy band may be due to overtones of the in-plane X-OH (Chamorro Pérez et al. 2006). The same weak bands appear in the IR spectrum of sample 4218 at practically the same wavenumbers, whereas in the spectrum of sample 3854 the band at \sim 3700 cm⁻¹ is not visible probably due to the very broad main absorption band. Also, the two extra bands at \sim 2900 cm⁻¹ in the spectrum of sample 3854 are likely due to some residual epoxy on the crystal surface. The main absorption bands of samples 3854 and 4218 are clearly at higher wavenumbers than the main OH-absorption bands of hydrous Mg₂SiO₄ and iron-bearing ringwoodite (12 mol% Fe), which have absorbance peaks centered at 3105-3120 and 3140 cm⁻¹, respectively (Boffa-Casanova et al. 2000; Smyth et al. 2003).

Equations of state

The variation of the unit-cell volumes of samples 3854 and 4218 is shown as a function of pressure in Figure 4. The continuous trend of the compression data indicates that no phase transition occurs for both samples in the investigated pressure range. The plot of normalized stress $F_E = P/3 f_E (1+2f_E)^{5/2}$ vs. Eulerian strain $f_{\rm E} = [(V_0/V)^{2/3} - 1]/2$ (Angel 2000) (Figs. 5a and 5b) has a horizontal slope indicating that the first pressure derivative of the bulk modulus, K', has a value of 4. Accordingly, the P-V data were fitted with a second-order Birch-Murnaghan EoS using the EOSFIT 5.2 program (Angel 2002) refining simultaneously

V (ų)



FIGURE 2. M-O distances (**a**) and T-O distances (**b**) of hydrous ringwoodite as a function of magnesium number; solid symbols = hydrous ringwoodite [Kudoh et al. (2000), 2 wt% H₂O; Smyth et al. (2003), 0.74 wt% H₂O Fo₁₀₀-ringwoodite, 0.86 wt% H₂O Fo₉₀-ringwoodite, 1.07 wt% H₂O Fo₈₇-ringwoodite]; open symbols = anhydrous ringwoodite; solid line = linear fit of anhydrous samples; dotted line = linear fit of hydrous samples.



FIGURE 3. Infrared spectra of hydrous ferroan ringwoodites; main absorption band is associated to protonation of octahedral sites and weaker absorption bands correspond to different types of OH-groups (Bolfan-Casanova et al. 2000).

the room-pressure unit-cell volume, V_0 , and the bulk modulus, K_{T0} . The refined EoS parameters are: $V_0 = 543.32(8)$ Å³ and $K_{\text{T0}} = 186.5(9)$ GPa for run 3854 and $V_0 = 539.01(5)$ Å³ and $K_{\text{T0}} = 184.1(7)$ GPa for run 4218. A third-order Birch-Murnaghan EoS fit of the *P-V* data yields the same results given the uncertainties i.e., $V_0 = 543.2(7)$ Å³, $K_{\text{T0}} = 189(4)$ GPa, and K' = 3.4(8) for run 3854 and $V_0 = 539.01(6)$ Å³, $K_{T0} = 185(3)$ GPa, and K' = 3.9(7) for run 4218.

DISCUSSION

Effect of hydrogen and Fe substitution on the Mg₂SiO₄ ringwoodite structure

The two Fe-bearing ringwoodite samples synthesized for this study differ not only in the water content, but also in their amount of Fe³⁺/ Σ Fe ratio (Table 1). The large amount of Fe³⁺ and relatively small amount of water of sample 4218 should result in a considerable amount of octahedral vacancies due to the oxidation of iron, which is not balanced by the protonation of oxygen (McCammon et al. 2004). The uncertainties in the microprobe analysis are such that it is difficult to discriminate whether or not octahedral vacancies are present. However, there is a clear indication from the structural refinements that



FIGURE 4. Variations of the unit-cell volumes of ferroan ringwoodites as a function of pressure. The values have been normalized with respect to the measured volumes at room pressure: solid line = fitted equation of state for run 4218; dotted line = fitted equation of state for run 3854.



FIGURE 5. Plot of Eulerian strain f vs. normalized stress F. The solid line represents a linear regression fit of data with the zero-pressure bulk modulus given by the F-axis intercept at zero-pressure: (a) run 3854, interception at 187.9 GPa; (b) run 4218, interception at 184.5 GPa.

these are indeed more frequent in sample 4218 and cannot be exclusively due to H incorporation. The Fe³⁺-related cation vacancies, however, appear to have only little effect on the unitcell volume of ringwoodite (Fig. 1). This is in contrast to what is reported for non-stoichiometric spinel (Nestola et al. 2009), which has a much smaller unit-cell volume than stoichiometric spinel (Nestola et al. 2007). There is some evidence, at least for the Mg₂SiO₄-ringwoodite end-member that H incorporation increases the unit-cell volume (Smyth et al. 2003). Our hydrous samples lie above the straight line connecting the anhydrous end-members (Fig. 1) suggesting that this trend is also valid for iron-rich ringwoodites.

The octahedral bond distance increases with increasing iron content (Fig. 2a) and appears only slightly affected by the H incorporation. In contrast, the T-O distance appears to have the same value for anhydrous Mg_2SiO_4 and Fe_2SiO_4 ringwoodites, but increases with increasing H content (Fig. 2b) (Smyth et al. 2003). An increase of the T-O bond distance has also been attributed by Hazen et al. (1993) to Mg/Si disorder between the octahedral and tetrahedral site. However, the water content of the samples studied by Hazen et al. (1993) was not measured and therefore it is difficult to assess the real effect of Mg/Si disorder, given that it is very difficult to determine with confidence from X-ray diffraction data due to the close similarity of the scattering curves of Si and Mg.

Effect of iron substitution on the OH-stretching mode of hydrous ringwoodite

The position of the main absorption band in the IR spectra of hydrous ringwoodites shift toward higher wavenumbers with increasing Fe content (Fig. 3).

The OH-stretching frequency depends on the bond strength of the O-H…O bond. With increasing iron content the bond strength A-H···B changes from strong to weak bonds according to the classification given by Emsley (1980). Weak bonds are defined as those with reduced proton transfer between atom A and B, i.e., with the hydrogen atom remaining covalently bonded to the parent atom A. This causes the shift of the OH-stretching frequencies to higher wavenumber since the interaction between H.B is reduced. Weaker hydrogen bonds i.e., higher OHstretching wavenumbers, are observed when the bond distance O···O increases (Libowitzky and Beran 2004). The structure refinement of ferroan ringwoodite (this study) indicates no change in O-O distance of the tetrahedral site with respect to the Mg₂SiO₄-ringwoodite end-member (2.70–2.71 Å) (Sasaki et al. 1982; Kudoh et al. 2000; Smyth et al. 2003), but an increase of the O-O distance for both the shared and unshared edges of the octahedral sites (Table 2). Hydrogen defects may be introduced into the ringwoodite structure by creating Mg or Si vacancies. Both tetrahedral edge (Smyth et al. 2003; Chamorro Pérez et al. 2006) and octahedral edge (Kudoh et al. 2000; Ross et al. 2003) have been suggested as the most probable protonation site. Recent theoretical studies (Blanchard et al. 2009; Li et al. 2009) found that based on energy consideration the Mg-substitution by two protons is the most favorable protonation mechanism, although Li et al. (2009) suggest that both type of defects are abundant in synthetic samples. In the present study, the presence of octahedral site vacancies as indicated from structural refinements as well as the correlation between the O-O octahedral edge and the wavenumber shift of the OH-mode (Fig. 6) point to the octahedral site as the most likely protonation site.

It also appears that the presence of ferric iron and the resulting cation vacancies have a strong effect on the OH-stretching frequencies since the absorption maximum of run 4218 Fo_{60} ringwoodite with 13% ferric iron is located at 3300 cm⁻¹ (Fig. 3), i.e., at larger wavenumber than that of run 3854 Fo_{50} -ringwoodite, which has purely ferrous iron.

Effect of hydrogen and Fe substitution on the compressibility of Mg₂SiO₄ ringwoodite

The bulk moduli of hydrous ferroan ringwoodites obtained in this study are very similar $[K_{T0} = 186.5(9) \text{ and } K_{T0} = 184.1(7)$ GPa for samples 3854 and 4218, respectively] and have values close to those reported for dry Mg-ringwoodite (Table 4). Hazen (1993) reports for Fe₆₀, Fe₈₀, and end-member Fe₁₀₀-ringwoodites values of bulk moduli ranging between 203 and 207 GPa with a K' fixed to the value of 4.8. For comparison, we also have used a Birch-Murnaghan EoS with K' fixed to the value of 4.8 to fit our *P-V* data with resulting EoS parameters: $V_0 = 543.38(8)$ Å³ and $K_{T0} = 183.1(9)$ GPa for run 3854 and $V_0 = 539.05(6)$ Å³ and $K_{\rm T0} = 181.0(7)$ GPa for run 4218. Thus our samples appear to be more compressible than the ferroan ringwoodites studied by Hazen (1993). There is some evidence that vacancies associated with the H incorporation strongly increase the compressibility of Mg₂SiO₄ ringwoodite (Table 4). If we assume that the samples studied by Hazen (1993) were anhydrous ferroan ringwoodites, the decrease of the bulk moduli values observed in our samples may be a consequence of the presence of vacancies. This suggestion is also supported by the fact that the sample 4218, which



FIGURE 6. Correlation between the OH-stretching wavenumber and the O-O distance of the octahedral shared edge; solid circles = Smyth et al. (2003); stars = this study.

Phase	H ₂ O (wt%)	Mg no.	K _{то} (GPa)	K' (dK/dP)	Method	P _{max} (GPa)	Reference
Ringwoodite							
	-	100	185(3)		BS		Jackson et al. 2000
	-	100	185(2)	4.5(2)	US	12	Li 2003
	-	100	184(2)		BS		Weidner et al. 1984
	-	100	199(9)	4.19	theory*	30	Kiefer et al. 1997
	-	92	188(3)	4.1(2)	BS	16	Sinogeikin et al. 2003
	-	100	184(2)	4.8(fixed)	XRD	5	Hazen 1993
	-	40	203(2)	4.8(fixed)	XRD	5	Hazen 1993
	-	20	205(2)	4.8(fixed)	XRD	5	Hazen 1993
	-	0	207(3)	4.8(fixed)	XRD	5	Hazen 1993
Hydrous ringwoodite							
	2.3	100	165.8(5)		BS		Wang et al. 2003
	2.2	100	155(4)		BS		Inoue et al. 1998
	~1	88	176(7)		US		Jacobsen et al. 2004
	~1	88	177(4)	5.3(4)	US	9	Jacobsen and Smyth 2006
	~1	88	175(3)	6.2(6)	XRD	45	Manghnani et al. 2003
	0.93	89	169(3)	7.9(9)	XRD	11.2	Smyth et al. 2004
run 4218	~0.4	61	184.1(7)	4 (fixed)	XRD	8.9	this study
run 3854	~0.7	49	186.5(9)	4 (fixed)	XRD	8.8	this study
Spinel phase							
Fe ₃ O ₄			185.7(3.0)	5.1(1)	US	8.7	Reichmann and Jacobsen 2004
MgAl ₂ O ₄			193(1)	5.6(3)	XRD	7.5	Nestola et al. 2007
^T (Mg _{0.4} Al _{0.6}) ^M (Al _{1.8} D _{0.2})O ₄			171(2)	7.3(6)	XRD	8.7	Nestola et al. 2009
* Calculated using plane	e-wave pseudopo	tential method.					

TABLE 4. Compressibility of ringwoodite and spinel phases

has the larger amount of vacancies due to iron oxidation, is also slightly more compressible than sample 3854. A strong increase in compressibility associated with the presence of octahedral vacancies has also been observed for non-stoichiometric MgAl₂O₄ spinel (Nestola et al. 2009). Recent theoretical study by Li et al. (2009) predicts a linear decrease of bulk modulus with increasing water content of ringwoodite i.e., an increasing amount of octahedral vacancies. Ferroan ringwoodite with up to 0.71 wt% H₂O (this study), however, does not show the predicted increase in compressibility within the analytical accuracy.

However, a recent study on Fe₂SiO₄-ringwoodite (Nestola et al. submitted to PEPI) reports a value of bulk modulus very similar to that of (Mg,Fe)₂SiO₄-ringwoodite examined in this study, suggesting, therefore, that the Fe-substitution has little effect on the compressibility of ringwoodite. This would suggest therefore that the oxygen closed-packing of the spinel structure is the decisive parameter in determining its compressibility and this cannot be affected by the presence of <1 wt% of water or of up to 0.1 atoms per formula unit of vacancies.

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