Effect of water on the sound velocities of ringwoodite in the transition zone

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High-pressure elasticity studies will play a central role in efforts to constrain the potential hydration state of the Earth's mantle from seismic observations. Here we report the effects of 1 wt% H₂O (as structurally bound OH) on the sound velocities and elastic moduli of single-crystal ringwoodite of Fo₉₀ composition, thought to be the dominant phase in the deeper part of the transition zone between 520 and 660-km depth. The experiments were made possible through development of a GHz-ultrasonic interferometer used to monitor *P* and *S*-wave travel times through micro-samples (30-50 μm thickness) under hydrostatic compression in the diamond-anvil cell. The velocity data to ~10 GPa indicate that hydrous ringwoodite supports 1-2% lower shear-wave velocities than anhydrous ringwoodite at transition zone pressures, though elevated pressure derivatives ($K' = 5.3 \pm 0.4$ and $G' = 2.0 \pm 0.2$) bring calculated hydrous *P*-velocities close to anhydrous values within their mutual uncertainties above ~12 GPa. Corresponding V_P/V_S ratios are elevated by ~2.3% and not strongly dependent on pressure. Velocities for hydrous ringwoodite are calculated along a 1673 K adiabat using finite-strain theory and compared with existing data on anhydrous ringwoodite and various radial seismic models. It may be possible to distinguish hydration from temperature anomalies by low *S*-velocities associated with "normal" *P*-velocities and accompanying high V_P/V_S ratios. The presence of a broadened and elevated 410-km discontinuity, together with depressed 660-km discontinuities and intervening low *S*-wave anomalies along with high V_P/V_S ratios are the most seismologically diagnostic features of hydration considering the available information from mineral physics.

1. Introduction

Based on the composition of primitive meteorites and the volatile content of igneous rocks, *Ringwood* [1966] recognized that the bulk Earth may contain three to five times the amount of hydrogen currently present in the atmosphere, hydrosphere, and sediments. Wadsleyite and ringwoodite (β , and γ - Mg_2SiO_4) display an unusual affinity for hydrogen, and together may be storing more H_2O by mass in the mantle transition zone (at 410-660 km depth) than is present in all the oceans combined [e.g. *Smyth*, 1987, 1994; *Inoue et al.*, 1995; *Kohlstedt et al.*, 1996; *Bolfan-Casanova et al.*, 2000]. The transition zone may therefore play a critical role in maintaining a global deep-Earth water cycle [*Kawamoto et al.*, 1996; *Bercovici and Karato*, 2003; *Ohtani et al.*, 2004; *Hirschmann et al.*, 2005; *Karato et al.*, *this volume*]. Since the transition zone partly controls heat and mass transfer between the lower and upper mantle, the presence of water in this region may influence conductive and radiative transport properties [*Karato*, 1990; *Huang et al.*, 2005; *Hofmeister*, 2004; *Keppler and Smyth*, 2005], rheology [*Karato et al.*, 1986; *Mei and Kohlstedt* 2000; *Kavner*, 2003] and mantle convection [*Richard et al.*, 2002; *Bercovici and Karato*, 2003].

The colloquial use of "water" or "hydration" of mantle minerals refers to the incorporation of hydrogen as structurally bound hydroxyl (OH), typically associated with point defects such as cation vacancies, coupled substitutions involving trivalent cations (such as aluminum), or reduction of ferric iron (Fe^{3+}) [*Kudoh et al.*, 1996; *Smyth et al.*, 2003; *McCammon et al.*, 2004; *Blanchard et al.*, 2005]. Because hydration leads to modified (i.e. defect) structures, an understanding of the influence of water on the elastic properties and sound velocities of nominally anhydrous mantle phases is needed to interpret seismological observation in regions of a potentially hydrous transition zone [e.g. *van der Meijde et al.*,

2003; Song *et al.*, 2004; Blum and Shen, 2004]. Equation of state parameters used in comparing laboratory mineral physics data with seismology include the initial density (ρ_0), thermal expansivity (α_V), isothermal and adiabatic bulk moduli (K_T , K_S) and the shear modulus (G , sometimes written μ). In addition, pressure and temperature derivatives of the moduli $K' = (dK/dP)_T$, $G' = (dG/dP)_T$, $(dK/dT)_P$ and $(dG/dT)_P$ are required to extrapolate compressional and shear-wave velocities (V_P , V_S) to deeper mantle conditions using finite-strain equations of state [e.g. Duffy and Anderson, 1989].

Ringwoodite is the high-pressure polymorph of olivine thought to be the dominant phase in the lower part of the transition zone (TZ) between about 520 and 660-km depth. Ringwoodite is known to incorporate 1.0-2.8 wt% H₂O at TZ conditions [Kohlstedt *et al.*, 1996; Inoue *et al.*, 1998; Smyth *et al.*, 2003], though hydration mechanisms remain uncertain. Infrared (IR) spectra are characterized by a broad absorption band at 2700-3800 cm⁻¹, typical of OH stretching. A strong band at ~1600 cm⁻¹, which could result from molecular H₂O are present in both hydrous and anhydrous samples and has therefore been interpreted as an overtone of the strong 800 cm⁻¹ Si-O stretching [Bolfan-Casanova *et al.*, 2000]. Single-crystal X-ray structure refinements of hydrous ringwoodite show predominantly octahedral-site vacancies and some Mg-Si disorder [Kudoh *et al.*, 2000; Smyth *et al.*, 2003], but classical atomistic simulations indicate that hydrogen associated with tetrahedral vacancies should be energetically favorable over other negatively charged point defects [Blanchard *et al.*, 2005]. Hydration leads to a positive volume change, lowering the density of ringwoodite (with $X_{Fe} \approx 0.10$) from 3700 (± 5) kg/m³ [Sinogeikin *et al.*, 2003] to 3650 (± 5) kg/m³ with ~1 wt% H₂O [Jacobsen *et al.*, 2004], representing about 1.4% density decrease upon hydration at 300 K and room pressure. Thermal expansion data from high-temperature X-ray diffraction studies

at room pressure are available for pure-Mg ringwoodite [Suzuki *et al.*, 1979] and hydrous pure-Mg ringwoodite [Inoue *et al.*, 2004]. Thermal expansivity at high pressure has been obtained by fitting P - V - T X-ray diffraction data for anhydrous pure-Mg ringwoodite [Meng *et al.*, 1994; Katsura *et al.*, 2004] and anhydrous iron-bearing ringwoodite [Nishihara *et al.*, 2004], but not hydrous ringwoodite. The comparative thermal expansion study of Inoue *et al.* [2004] indicates that α_V is $\sim 10\%$ lower in hydrous ringwoodite compared with anhydrous ringwoodite. Static compression studies at 300 K have been carried out on γ -Mg₂SiO₄, γ -(Mg_{0.6}Fe_{0.4})₂SiO₄, γ -(Mg_{0.4}Fe_{0.6})₂SiO₄, γ -(Mg_{0.2}Fe_{0.8})₂SiO₄ and γ -Fe₂SiO₄ spinels [Hazen, 1993; Zerr *et al.*, 1993]. For comparison, compressibility studies of hydrous pure-Mg ringwoodite [Yusa *et al.*, 2000] and hydrous Fe-bearing ringwoodite [Smyth *et al.*, 2004; Manghnani *et al.*, 2005] indicate that K_{T0} is reduced by 8-10% upon hydration, meaning that hydrous ringwoodite is more compressible than anhydrous ringwoodite. While the various P - V - T datasets obtain α_V , K_{T0} , K' and dK/dT needed to estimate mineral densities in the transition zone, they do not provide direct information on the adiabatic elastic wave velocities, V_P and V_S .

The elastic properties of ringwoodite have been studied by various techniques including Brillouin spectroscopy [e.g. Sinogeikin *et al.*, 2003], ultrasonic interferometry [e.g. Li, 2003], the resonant sphere technique [Mayama *et al.*, 2005], radial X-ray diffraction [Kavner, 2003; Nishiyama *et al.*, 2005] and computational methods [e.g. Kiefer *et al.*, 1997]. Room pressure Brillouin studies have determined the single-crystal elastic constants (C_{ij}) of anhydrous pure-Mg ringwoodite [Weidner *et al.*, 1984], anhydrous Fe-bearing ringwoodite [Sinogeikin *et al.*, 1998], and hydrous pure-Mg ringwoodite [Inoue *et al.*, 1998; Wang *et al.*, 2003]. The C_{ij} are symmetry reduced elements of the fourth-rank tensor (C_{ijkl}) relating stress and strain in

Hooke's law [Nye, 1972] and are useful in calculating elastic anisotropy as well as K_S and G from polycrystalline averaging schemes [Hashin and Strikman, 1962]. The C_{ij} of Fe-bearing hydrous ringwoodite were determined ultrasonically at room P - T conditions [Jacobsen *et al.*, 2004]. Together, these studies indicate adding $\sim 10\%$ iron to pure-Mg ringwoodite leaves K_S and G unchanged within experimental uncertainties, but the addition of 1-2 wt% H_2O to either pure-Mg or Fe-bearing ringwoodite reduces K_S by 6-9% and G by 9-13%. Temperature derivatives of the elastic moduli for pure-Mg and Fe-bearing anhydrous ringwoodite have been obtained by Brillouin spectroscopy [Jackson *et al.*, 2000; Sinogeikin *et al.*, 2003] and the resonant sphere techniques [Mayama *et al.*, 2005]. Temperature derivatives of the elastic moduli for hydrous ringwoodite are not yet available. Pressure derivatives of the elastic moduli for anhydrous pure-Mg ringwoodite have been obtained ultrasonically [Li, 2003] and for anhydrous Fe-bearing ringwoodite by Brillouin spectroscopy [Sinogeikin *et al.*, 2003].

Though structurally bound hydroxyl is readily detectable in laboratory samples using IR spectroscopy, can hydration of the mantle transition zone be detected seismically in the real Earth? In order to address this question, efforts are underway to quantify the effects of hydration on the physical properties of the major nominally anhydrous mantle phases. In this study, we have determined the pressure dependence of the C_{ij} , aggregate moduli (K_S , G) and sound velocities of hydrous ringwoodite with Fo₉₀ composition containing about 1 wt% of H_2O to 9.2 GPa. Finite strain theory is used to calculate compressional and shear-wave velocities at transition zone pressures and 300 K. Using some assumptions about temperature derivatives of the elastic moduli for hydrous ringwoodite, we also estimate monomineralic velocities along a 1673 K adiabat for comparison with anhydrous ringwoodite and various radial seismic models.

2. Experiment

2.1 Sample Synthesis and Characterization

Hydrous ringwoodite was synthesized at 20 GPa and 1400°C in the 5000-ton multianvil press at Bayerisches Geoinstitut. The sample corresponds to run SZ9901 in our previous X-ray diffraction studies [Smyth *et al.*, 2003; Smyth *et al.*, 2004]. A large 18/11 assembly [Frost *et al.*, 2004] consisting of an 18-mm edge-length MgO octahedron for 54-mm carbide cubes with 11-mm truncations was used to compress a 2.0-mm welded-Pt capsule fitted with a stepped lanthanum chromate heater. The large capsule size in this assembly may facilitate the growth of large crystals, which measured up to 800 μm in this experiment. Starting materials consisted of natural Fo₉₀ olivine, En₉₀ orthopyroxene, hematite, and silica, with ~3 wt% water was added as brucite. Heating duration was five hours. The crystals are deep-blue in color and have approximate composition $\gamma\text{-(Mg}_{0.85}\text{Fe}_{0.11})_2\text{H}_{0.16}\text{SiO}_4$ from microprobe analysis [Smyth *et al.*, 2003]. Mössbauer and Electron Energy Loss Spectroscopy using TEM [Smyth *et al.*, 2003] indicate that approximately 10% of the iron is ferric (i.e. $\text{Fe}^{3+}/\Sigma\text{Fe} = 0.10$). Single-crystal samples were oriented on crystallographic vectors [100], [110], and [111] with a four-circle X-ray diffractometer and parallel polished into platelets measuring between 30 and 50 μm in thickness. IR-spectroscopy was carried out on the ultrasonic samples showing approximately 0.96-1.01 wt% H₂O [Jacobsen *et al.*, 2004] using the calibration of Paterson [1982]. Unlike olivine [Bell *et al.*, 2003], an absolute calibration for water is not available for ringwoodite, so the accuracy of the measured water content is not known and can only be directly compared with other studies using infrared spectroscopy. Single-crystal X-ray diffraction of the ultrasonic samples gives a cubic unit-cell volume of 530.80(5) $\text{\AA}^3$ for a calculated density of $\rho_0 = 3.651(5) \text{ g/cm}^3$.

2.2 Gigahertz-ultrasonic interferometry

High-pressure ultrasonic measurements were carried out in a diamond-anvil cell using GHz-ultrasonic interferometry [Spetzler *et al.*, 1993; Jacobsen *et al.*, 2005]. Diamond cells typically require samples less than ~ 100 μm thick in order to achieve pressures above ~ 5 GPa. The wavelength of strain waves is given by $\lambda = V/f$, where V is the velocity and f is the frequency. In mantle minerals where $V_P \sim 10$ km/s and $V_S \sim 5$ km/s, acoustic wavelengths at 10-100 MHz with commercial transducers are typically 0.1 to 1.0 mm, being much too long for interferometric techniques with diamond-cell samples. By driving ultrasonic transducers at 0.5 to 2 GHz, acoustic wavelengths are reduced to ~ 5 -10 μm , suitable for ultrasonics in the diamond cell. P -waves are generated by thin-film, zinc-oxide transducers sputtered directly onto an acoustic buffer rod. In separate experiments, S -waves are generated by P -to- S conversion inside a single-crystal acoustic buffer rod before transmission into the diamond cell. Shear waves produced in this way are purely polarized, given by the polarization direction of the incident P -wave. Details of the new GHz-ultrasonic technique with both P - and S -wave capabilities are given elsewhere [Jacobsen *et al.*, 2004; Jacobsen *et al.*, 2005]. Hydrostatic pressures were maintained to the maximum pressure of 9.2 GPa using a 16:3:1 methanol:ethanol:water pressure transmitting medium.

2.3 Data analysis and equation of state fitting procedures

Ringwoodite is cubic (space group $Fd3m$, spinel structure) and has three unique single-crystal elastic constants (C_{11} , C_{44} , C_{12}). The elastic constants were determined from P - and S -wave travel times (t_P , t_S) along the crystallographic vectors $[100]$, $[110]$, and $[111]$. Four different pure-mode velocities were used to determine the C_{ij} as follows:

$$\rho(V_P^{[100]})^2 = C_{11} \quad (1)$$

$$\rho(V_S^{[100]})^2 = C_{44} \quad (2)$$

$$\rho(V_P^{[110]})^2 = 1/2(C_{11} + 2C_{44} + C_{12}) \quad (3)$$

$$\rho(V_S^{[111]})^2 = 1/3(C_{11} + C_{44} - C_{12}) \quad (4)$$

In equations (1) through (4), the superscript $[uvw]$ to each velocity gives the direct-space vector of wave propagation, which is parallel to the wave polarization for V_P . For $V_S^{[100]}$ and $V_S^{[111]}$, the shear-wave polarization is degenerate. Velocities were calculated from the measured travel times using the relation $V_{P,S} = (2l/t_{P,S})$, where l is the sample length, initially determined by micrometer measurements to $\pm 1 \mu\text{m}$ [Jacobsen *et al.*, 2004]. The change in sample length with pressure was calculated using third-order Birch Murnaghan equation of state parameters $K_{T0} = 175(3) \text{ GPa}$ and $K' = 6.2(6)$, determined by separate static compression experiments on hydrous ringwoodite to 45 GPa [Manghnani *et al.*, 2005]. The choice of K' in the length calculation is not critical over the experimental pressure range. The difference in calculated length at 10 GPa using $K' = 6.2$ versus $K' = 4.0$ is only 0.06-0.10% (for 30-50 μm initial length). The resulting difference in velocity at 10 GPa is only about 5 m/s, which is considerably smaller than the typical uncertainty in velocity due to standard deviation in the travel times (a few parts in 10^3). Thus, errors in the reported velocities and elastic constants (Tables 1-4) are dominated by errors in the measured travel times. We distinguish absolute accuracy in the room pressure values, dominated by uncertainty in the length [Jacobsen *et al.*, 2004], with relative uncertainties at high pressure, dominated by uncertainty in the travel-times and change in length and used for the purpose of equation of state fitting. Pressures were obtained with the ruby-fluorescence scale [Mao *et al.*, 1986] and carry a nominal uncertainty of $\pm 0.05 \text{ GPa}$.

Compressional and shear-wave velocities in various crystallographic directions of hydrous ringwoodite are plotted in Figure 1. The velocities were used to calculate C_{ij} using equations (1)-(4). Both C_{11} and C_{44} were determined directly by $V_P^{[100]}$ and $V_S^{[100]}$ respectively. C_{12} was determined in two separate experiments using $V_P^{[110]}$ and $V_S^{[111]}$. These velocities give a linear combination of elastic constants shown in equations (3)-(4), which were solved independently for C_{12} at their respective experimental pressures using linear fits to C_{11} and C_{44} given in Table 5. Therefore, equations (3) and (4) provide an independent cross-check of C_{12} since it is determined by two separate experiments involving two different crystallographic directions, in one case with P -waves and in the other case S -waves. Variation of the elastic constants with pressure for Fe-bearing hydrous ringwoodite is plotted in Figure 2, along with linear fits to C_{ij} for nominally anhydrous Fe-bearing ringwoodite measured by *Sinogeikin et al.* [2003].

Aggregate elastic moduli and acoustic velocities were determined using the Voigt-Reuss-Hill (VRH) averaging scheme [*Hill, 1952*]:

$$C_S = \frac{(C_{11} - C_{12})}{2} \quad (5)$$

$$G_R = \frac{(5C_S C_{44})}{(2C_{44} + 3C_S)} \quad (6)$$

$$G_V = \frac{(2C_S + 3C_{44})}{5} \quad (7)$$

$$G_{VRH} = \frac{G_R + G_V}{2} \cong G = \rho(V_S)^2 \quad (8)$$

$$K_S = \frac{(C_{11} + 2C_{12})}{3} = \rho(V_P)^2 - \left(\frac{4}{3}\right)G \quad (9)$$

While the approach of *Hashin and Strikman* [1962] has been shown to place tighter bounds on the shear modulus, in this case the difference between the Voigt bound (G_V) and Reuss bound (G_R) was typically 0.5% or less, so the simpler VRH approach was employed. At each pressure where C_{44} was determined directly, K_S , G , and the acoustic velocities were determined using linear fits to C_{11} and C_{12} and equations (8) and (9). The aggregate acoustic velocities at high pressure (Table 6) were fitted to a third-order finite strain equation of state [Davies and Dziewonski, 1975; Duffy and Anderson, 1989] using the following formulation:

$$\rho(V_P)^2 = (1 - 2\varepsilon)^{5/2} (L_1 + L_2\varepsilon) \quad (10)$$

$$\rho(V_S)^2 = (1 - 2\varepsilon)^{5/2} (M_1 + M_2\varepsilon) \quad (11)$$

$$P = -(1 - 2\varepsilon)^{5/2} \left(C_1\varepsilon + \frac{C_2(\varepsilon^2)}{2} \right) \quad (12)$$

where strain (ε) is $^{1/2}[1 - (\rho/\rho_0)^{2/3}]$. Finally, equation of state parameters K_0 , G_0 , K' and G' were determined from the finite strain fitting parameters using:

$$M_1 = G_0 \quad (13)$$

$$L_1 = K_0 + (^{4/3})G_0 \quad (14)$$

$$C_1 = 3L_1 - 4M_1 \quad (15)$$

$$M_2 = 5G_0 - K_0G' \quad (16)$$

$$L_2 = 5(K_0 + (^{4/3})G_0) - 3K_0(K' + (^{4/3})G') \quad (17)$$

$$C_2 = 3L_2 - 4M_2 + 7C_1 \quad (18)$$

3. Results and Discussion

3.1 Elastic moduli of hydrous iron-bearing ringwoodite

Jacobsen et al. [2004] determined the single-crystal elastic constants and aggregate moduli of hydrous ringwoodite (Fo₉₀ composition) at room P - T conditions using the same samples measured in the current high-pressure study. They reported $C_{11} = 298(13)$, $C_{44} = 112(6)$, $C_{12} = 115(6)$ GPa, where the errors in parentheses reflect the absolute accuracy of the measurements, dominated by uncertainty in sample thicknesses. These values are in agreement with C_{ij} obtained by linear fits (Table 5) to the variation of C_{ij} with pressure in the current study; $C_{11} = 299(3)$, $C_{44} = 112.2(5)$, and $C_{12} = 116.2(4)$ GPa, where errors in parentheses reflect error-weighted regressions dominated by the measured travel times and change in sample length as described above. VRH averaged moduli from *Jacobsen et al.* [2004] are $K_{S0} = 176(7)$, and $G_0 = 103(5)$, in agreement with the current high-pressure study where third-order finite strain fitting to the ρV^2 data (Table 6) yields $K_{S0} = 177(4)$ and $G_0 = 103.10(9)$ GPa, with $K' = 5.3(4)$ and $G' = 2.0(2)$. Errors in the equation of state parameters were calculated from errors in the fitting parameters L_1 , L_2 , M_1 , M_2 (Eq. 10-11) from experimental error in travel times, density, and length change.

Upon hydration to ~1 wt% H₂O, all of the single-crystal moduli are reduced by variable amounts compared with anhydrous Fe-bearing ringwoodite measured by Brillouin spectroscopy [*Sinogeikin et al.*, 2003], with $C_{11} = 329(3)$, $C_{44} = 130(1)$, and $C_{12} = 118(2)$. From this comparison, C_{11} and C_{44} are reduced by 9.4% and 13.8% respectively, whereas the C_{12} is lowered by only about 2.5%. Aggregate moduli from the anhydrous Fe-bearing ringwoodite study are $K_{S0} = 188(3)$ and $G_0 = 120(2)$ GPa. Thus, hydration to 1 wt% H₂O lowers K_{S0} and G_0 by about 6% and 13%, respectively. The reduction in moduli upon hydration was used to estimate the effect of water on aggregate velocities [*Jacobsen et al.*, 2004], resulting in -42 m/s and -36 m/s (V_P and V_S respectively) for every 0.1 wt% H₂O

(1000 ppm wt.% H₂O) added to Fe-bearing ringwoodite at room pressure. To illustrate the magnitude of this effect, we note that in consideration of measured temperature derivatives for anhydrous ringwoodite in Table 7 [Sinogeikin *et al.*, 2003], the addition of ~1 wt% of water is equivalent to raising the temperature, in terms of V_P and V_S reduction, by about 600 and 1000 °C respectively. At low pressure, hydration of ringwoodite has a larger effect on the velocities than temperature within possible ranges of these parameters in the mantle. In this study, we incorporate the effects of water on measured pressure derivatives, and will revisit the effects of water on V_P and V_S at TZ conditions in section 3.4.

3.2 Elastic moduli of hydrous iron-bearing ringwoodite at high pressure

Pressure derivatives of all the C_{ij} are markedly higher upon hydration (Table 5, Figure 2) in comparison with anhydrous Fe-bearing ringwoodite [Sinogeikin *et al.*, 2003]. The pressure derivative of C_{11} is 8.3(5) for hydrous ringwoodite compared with 6.2(2) for anhydrous ringwoodite. The pressure derivative of C_{44} is 1.37(8), compared with 0.8(2) for anhydrous ringwoodite, and dC_{12}/dP is 3.38(8), compared with 2.8(3) for anhydrous ringwoodite. For anhydrous ringwoodite $C_{12} < C_{44}$ at room pressure, but because $dC_{12}/dP > dC_{44}/dP$ the term C_{12} crosses C_{44} at approximately 6 GPa (Figure 2). Upon hydration, the dramatic lowering of C_{44} from 130 to 112 GPa results in C_{12} being ~4 GPa higher than C_{44} . In these experiments, equations (3) and (4) represent an important redundancy check of C_{12} since it was determined in two separate experiments using the same direct measurements of C_{11} and C_{44} and from both V_P and V_S in different crystallographic directions. In fact, that $C_{12} > C_{44}$ at room pressure is typical for oxide spinels [Yoneda 1990; Reichmann and Jacobsen 2005], so it might be considered unusual that $C_{12} < C_{44}$ for anhydrous ringwoodite. In simple structures,

the relative values of C_{44} and C_{12} may provide some insight into the nature of interatomic bonding [*e.g. Weidner and Price, 1988*]. When interatomic forces are parallel to the relative position between atom pairs, the elastic constants satisfy an identity known as the Cauchy condition:

$$\frac{1}{2}(C_{12} - C_{44}) = P \quad (19)$$

where P is pressure. At room pressure, $\frac{1}{2}(C_{12} - C_{44}) = 2$ GPa for hydrous ringwoodite, being closer and of positive sign (like the other spinel structures) compared with that reported for anhydrous ringwoodite at room pressure [*Sinogeikin et al., 2003*], where $\frac{1}{2}(C_{12} - C_{44}) = -6$ GPa. Deviation from the Cauchy condition of about +2 and -6 GPa for hydrous and anhydrous ringwoodite respectively are maintained over the experimental pressure ranges.

The single crystal elastic constants of hydrous ringwoodite were used to calculate bulk and shear moduli as a function of pressure using equations (5) through (9), and are plotted together with results on anhydrous Fe-bearing ringwoodite and anhydrous pure-Mg ringwoodite in Figure 3. A third-order finite strain equation of state was fitted to the ρV^2 data in Table 6 resulting in pressure derivatives $K' = 5.3(4)$ and $G' = 2.0(2)$, compared with $K' = 4.1(3)$ and $G' = 1.3(2)$ for anhydrous Fe-bearing ringwoodite [*Sinogeikin et al., 2003*]. Reduced moduli, and elevated pressure derivatives measured ultrasonically in this study are consistent with the emerging trends for hydrous phases (of K_{T0} and K_T') determined in static compression studies with X-ray diffraction. For example in olivine, K_{T0} is reduced from ~129 GPa to 120 GPa with ~0.8 wt% H₂O, while $K' \sim 7$ compared with $K' \sim 5$ for dry olivine [*Smyth et al., 2005*]. Similarly for wadsleyite, anhydrous samples give $K_{T0} = 174(4)$ GPa with $K' = 3.9(11)$, and when hydrated to ~1 wt% H₂O, $K_{T0} = 152(6)$ GPa with $K' = 6.5(20)$ [*Holl et al., 2003*]. For ringwoodite, the current ultrasonic values $K_{S0} = 177(4)$ GPa with $K' = 5.3(4)$

are comparable to those obtained by static compression of hydrous ringwoodite (of Fo₉₀ composition) from X-ray diffraction with $K_{T0} = 175(3)$ GPa with $K' = 6.2(6)$ [Manghnani *et al.*, 2005]. The difference between measured adiabatic and isothermal values of K for hydrous Fe-bearing ringwoodite is consistent with isothermal-adiabatic transformations represented by the Grüneisen relation, $K_S = K_T(1 + \alpha\gamma_{th}T)$, for values of $\alpha = 2.7\text{-}3.0 \times 10^{-5} \text{ K}^{-1}$ [Inoue *et al.*, 2004] and thermal Grüneisen the coefficients (γ_{th}) of 1.2-1.5 [Poirier, 2000]. Though the adiabatic and isothermal K obtained ultrasonically and by static compression are in excellent agreement, the ultrasonic K' is about 15% lower. The reason for this discrepancy is unknown, but since K' is a third-order fitting parameter in the static compression studies, we consider the ultrasonic K' to be more accurate (i.e. since K is obtained at each pressure).

3.3 Velocities and anisotropy at high pressure and 300 K

Is it possible to detect the presence of water or variations in hydration at the level of ~1 wt% H₂O in the transition zone seismically? In order to evaluate the effect of water on aggregate sound velocities of ringwoodite at high pressures, third-order equation of state parameters (Table 7) and equations (10) and (11) were used to compare velocities of pure-Mg anhydrous ringwoodite [Li, 2003], anhydrous Fe-bearing ringwoodite [Sinogeikin *et al.*, 2003], and hydrous Fe-bearing ringwoodite from the current study at TZ pressures (Figure 4). Although initially (P_0 , 300 K) P -wave velocities are about 400($\pm$ 60) m/s (~4.0%) slower in hydrous ringwoodite, due to the elevated pressure derivatives of the moduli, V_P for hydrous ringwoodite is comparable within uncertainty to anhydrous ringwoodite above ~12 GPa. Therefore, in the depth range where ringwoodite is the stable phase (~18-24 GPa), we expect that the 300 K P -wave velocities for hydrous and anhydrous ringwoodite are indistinguishable (Figure 4).

Shear-wave velocities are initially (P_0 , 300 K) about 360($\pm$ 60) m/s ($\sim$ 6.7%) slower in hydrous Fe-bearing ringwoodite (Figure 4). Despite the elevated G' , and unlike V_P , the pronounced slowing of S -wave velocities upon hydration means that hydrous shear velocities remain lower than anhydrous V_S throughout TZ pressures. At 20 GPa, the calculated hydrous V_S is still 1-2% slower than anhydrous V_S .

Elastic wave anisotropy is a critical feature of seismic data typically associated with mantle flow [*e.g.* Karato, 1998]. Although evidence for anisotropy in the TZ is somewhat sparse, there are reports of observed anisotropy in the TZ associated with remnant subducted oceanic lithosphere beneath Fiji-Tonga [Chen and Brudzinski, 2003]. One way to quantify elastic anisotropy in cubic phases such as spinel is given by the anisotropy factor [Karki *et al.*, 1999]:

$$A = \left[\frac{2C_{44} + C_{12}}{C_{11}} \right] - 1 \quad (20)$$

where $A = 0$ for an elastically isotropic crystal. Despite the dramatic reduction of C_{44} compared with C_{11} and C_{12} upon hydration, the anisotropy factor of anhydrous Fe-bearing ringwoodite, $A = 0.15$ [Sinogeikin *et al.*, 2003], is indistinguishable with $A = 0.14(2)$ for hydrous Fe-bearing ringwoodite within error. Compared with other cubic phases like MgO ($A = 0.36(2)$ [Jacobsen *et al.*, 2002]), the anisotropy factor of ringwoodite is quite low anyway. The variation of A with pressure for anhydrous and hydrous ringwoodite is plotted together with MgO for comparison in Figure 5. Although the effects of temperature are neglected here, we suggest that anisotropy is not likely a useful indicator of hydration because A is so similar for anhydrous and hydrous ringwoodite, but also because both decrease to near zero at 16-25 GPa (Figure 5).

The most diagnostic difference between anhydrous and hydrous ringwoodite with respect to seismological observation is the V_P/V_S ratio and related Poisson's ratio (ν):

$$\nu = \frac{3K_S - 2G}{2(3K_S + G)} = \frac{1}{2} \frac{(V_P/V_S)^2 - 2}{(V_P/V_S)^2 + 1} \quad (21)$$

The V_P/V_S ratio of ringwoodite is elevated from 1.706(7) [Sinogeikin *et al.*, 2003] to 1.75(2) upon hydration, or about 2.3% higher. Elevated V_P/V_S ratios persist at high pressure, where above 14 GPa (and 300 K) the calculated V_P/V_S ratio of hydrous ringwoodite is still ~2.3% higher (Figure 6). Poisson's ratio of hydrous ringwoodite is 0.256(3), or ~8% higher than anhydrous ringwoodite with $\nu = 0.237(1)$. Above 14 GPa, the calculated Poisson's ratio of hydrous ringwoodite is still ~4.5% higher than anhydrous ringwoodite.

Hydration has a much stronger influence on V_P/V_S than temperature or variation in Fe-content within their respective possible variations in the transition zone. A high-temperature Brillouin study of γ -(Mg_{0.91}Fe_{0.09})₂SiO₄ indicates that V_P/V_S increases from 1.706 at 300 K to 1.712 at 923 K, a variation of just 0.4% over 628 K [Sinogeikin *et al.*, 2003]. The variation in V_P/V_S with Fe-content is indistinguishable within experimental uncertainties, with $V_P/V_S = 1.71(1)$ for pure-Mg ringwoodite [Li, 2003] compared with 1.706(7) for γ -(Mg_{0.91}Fe_{0.09})₂SiO₄ [Sinogeikin *et al.*, 2003]. The ~2% increase in V_P/V_S on hydration is maintained at high-pressure conditions, and is therefore the best seismic parameter to consider, especially where elevated V_P/V_S is associated with "normal" P -velocities and reduced S -velocities since elevated temperatures will reduce both V_P and V_S .

3.4 Calculation of hydrous velocities in the transition zone

In order to evaluate the effects of water on seismic velocities of ringwoodite in the transition zone, we calculated monomineralic V_P and V_S along a 1673 K adiabat using finite

strain theory for comparison with anhydrous ringwoodite and seismic models such as PREM [Dziewonski and Anderson, 1981] and IASPEI91 [Kennett and Engdahl, 1991]. Temperature derivatives of the moduli for hydrous ringwoodite are not available, so for the purpose of this calculation we chose to examine two different cases. In the first, we simply used the same temperature derivatives as for anhydrous ringwoodite [Sinogeikin *et al.*, 2003], given in Table 7. In the second case, we reduced dK/dT and dG/dT by an amount proportional to the product αK_T . Examination of a large number of elasticity data for oxide minerals indicates that the magnitude of temperature derivatives tends to increase by an amount proportional to this product [Duffy and Anderson, 1989]. Taking anhydrous $\alpha_V = 3.07 \times 10^{-5} \text{ K}^{-1}$ with $K_T = 186 \text{ GPa}$, and hydrous $\alpha_V = 2.73 \times 10^{-5} \text{ K}^{-1}$ with $K_T = 175 \text{ GPa}$ [Inoue *et al.*, 2004; Manghnani *et al.*, 2005], the product αK_T is reduced by about 15% in the hydrous case. Therefore, in the reduced derivative calculation we used $dK_S/dT = -0.024$ and $dG/dT = -0.018 \text{ GPa K}^{-1}$. Densities at high temperature were calculated using thermal expansivities of Inoue *et al.* [2004] given above. Moduli were then calculated at room pressure at the foot of a 1673 K adiabat using temperature derivatives for the two different cases. Finally, the high-temperature velocities were projected adiabatically into the transition zone using equations (10)-(12) with model parameters given in Table 7.

Monomineralic velocities for anhydrous and hydrous ringwoodite are plotted together with two seismic models in Figure 7. In the case where we have assumed the same temperature derivatives for anhydrous and hydrous ringwoodite, P -wave velocities for anhydrous and hydrous ringwoodite are within about 50 m/s ($\sim 0.5\%$) of each other between 520 and 660 km depth, and therefore are considered to be equal within their mutual uncertainties, and lie about 80 m/s ($\sim 0.8\%$) above PREM. When the temperature derivatives

of hydrous (or anhydrous) ringwoodite are reduced by 15% as described above, P -velocities match PREM very well between ~ 550 and 660 km depth. Hydrous S -wave velocities remain well below anhydrous V_S throughout the lower part of the transition zone and show a good fit to PREM. At 520 km-depth hydrous V_S is about 160 m/s ($\sim 2.9\%$) below anhydrous V_S and at 660 km depth hydrous V_S is about 100 m/s ($\sim 1.8\%$) below anhydrous V_S . When the temperature derivative of hydrous ringwoodite is varied by 15% as described above, hydrous S -velocities bound both PREM and IASPI91 models whereas anhydrous S -velocities lie about 135 m/s ($\sim 2.5\%$) above these models in the lower part of the transition zone. To summarize, hydrous and anhydrous P -velocities are indistinguishable at TZ conditions and are $\sim 1\%$ faster than PREM, whereas hydrous S -velocities are 2-3% slower than anhydrous S -velocities and match radial seismic models very well (Figure 7).

The V_P/V_S ratio of PREM at 600 km depth is 1.84, compared with 1.85 for hydrous ringwoodite and 1.81 for anhydrous ringwoodite in the current calculation, another indication that hydrous (monominerallic) ringwoodite velocities provide a better fit to radial seismic models. However, there are many uncertainties in the current comparison. Though our intention here is only illustrate the magnitude of effects of water on monominerallic velocities, the lower part of the transition zone is unlikely to be pure ringwoodite. The $(\text{Mg,Fe})\text{SiO}_3$ phase (majorite) is also likely to be present in various modal proportions depending on the mineralogical model [e.g. *Ringwood, 1975; Bass and Anderson, 1984*]. Majorite velocities are lower than PREM [see e.g. *Smyth and Jacobsen, this volume*] and could therefore also explain the discrepancy between (high) anhydrous V_P and V_S velocities and PREM. The comparison with PREM and IASPI91 also involves radially averaged seismic models, which do not reflect local variation in temperature or composition, both of

which should vary to some extent locally in the transition zone. Water, if present, may not be evenly distributed throughout the transition zone. Fractional melting (due to water) is yet another key parameter not treated here but expected to influence bulk sound velocities. Furthermore, we note that the velocities measured here at GHz frequencies are fully unrelaxed and do not reflect high-temperature dispersion or attenuation [e.g. *Jackson et al.*, 2005], and in particular the possible effects of water on high-temperature viscoelastic relaxation, which may act to reduce observed seismic (Hz) velocities further [e.g. *Karato and Jung*, 1998]. An additional uncertainty arises from the potential influence of second (pressure) derivatives, K'' and G'' , which currently are implied values from the third-order truncation. Data spanning a greater pressure range will be required to ascertain to what extent the observed elevated K' and G' may be offset at higher pressure due to increasing $|K''|$ and $|G''|$. However, we note that the crossing of hydrous K_S with anhydrous K_S (Figure 3) is only 2-3 GPa beyond the current measured data and therefore this unusual observation is fairly robust. We emphasize that the model is not a rigorous test of water in the transition zone, and is only meant to highlight the most important features of hydration for monomineralic ringwoodite velocities at high pressure.

4. Seismic structure of a hydrous transition zone

Identifying hydration, or lateral variation of hydration in the TZ will require several types of seismic data together with a comprehensive view of regional mantle structure. Here we have shown how hydration of ringwoodite could manifest itself in the lower part of the transition zone as "normal" P -velocities and reduced S -wave velocities accompanied by elevated V_P/V_S ratios at the level of several percent. The same is expected to be true for

wadsleyite in the upper part of the TZ, however, at the time of writing sound velocity data (even at room pressure) are not yet available for hydrous wadsleyite. Temperature derivatives of the elastic moduli, for both hydrous wadsleyite and hydrous ringwoodite are also needed.

Water is also expected to influence the width (depth interval) and absolute depth of the "410" and "660" seismic discontinuities. A discussion of the effects of water on the "410" structure is presented elsewhere [see *Hirschmann et al.*, this volume]. Briefly, the width of the two-phase loop between olivine and wadsleyite increases with increasing water content [Wood, 1995; Smyth and Frost, 2002], at least up to the point of saturation where a free fluid phase (melt) forms and the loop narrows again [Chen et al., 2002; Hirschmann et al., 2005], favoring a sharper seismic discontinuity. Despite the higher water storage capacity of olivine at conditions of ~410 km depth relative to shallow mantle conditions [e.g. Chen et al., 2002; Smyth et al., 2005], the partition coefficient of water between olivine and wadsleyite is still expected to be greater than unity, probably around 5 [Hirschmann et al., this volume].

Similarly, the storage capacity of water in ringwoodite is much higher than in the silicate perovskite at "660", probably by around 1000 times [Bolfan-Casanova et al., 2003].

Displacement of the "410" upwards and the "660" downwards due to the presence of water would therefore create a thick transition zone, i.e. with a greater depth interval between "410" and "660" compared with a nominally dry region. Thus, seismic studies for water should include high-resolution local velocity structure in candidate locations, preferably away from subduction zones where thermal anomalies are likely minimal. In the same regions, accurate transition zone structure (discontinuity depths and TZ thickness) will be needed. A locally thick transition zone could also occur due to an anomalously low temperature relative to the surrounding mantle, however, if intervening (especially *S*-wave) velocities are low and V_P/V_S

ratios high, the best compositional explanation appears to be H₂O. The presence of a broadened and elevated "410" discontinuity, together with depressed "660" discontinuity with intervening low *S*-wave anomalies and high V_P/V_S ratios would be highly compatible with hydration considering the available information from mineral physics.

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Figure Captions

Figure 1. Single-crystal velocities in various crystallographic directions of hydrous ringwoodite (Fo₉₀ composition) as a function of pressure measured by GHz-ultrasonic interferometry.

Figure 2. Single-crystal elastic constants of hydrous Fe-bearing ringwoodite as a function of pressure. C_{11} (filled diamonds) and C_{44} (filled circles) were determined by $V_P^{[100]}$ and $V_S^{[100]}$ directly using equations (1) and (2) in the text. C_{12} was determined in two separate experiments using $V_S^{[111]}$ (filled squares) and $V_P^{[110]}$ (open squares). Solid curves are linear fits (Table 5) to all the data. Variation of C_{ij} with pressure for anhydrous Fe-bearing ringwoodite from Brillouin spectroscopy [Sinogeikin *et al.*, 2003] is shown by grey curves.

Figure 3. Variation of the bulk (K_S) and shear (G) moduli with pressure for hydrous Fe-bearing ringwoodite (this study, filled symbols and solid lines), anhydrous Fe-bearing ringwoodite from Sinogeikin *et al.* [2003] (open symbols and grey solid lines), and anhydrous pure-Mg ringwoodite from Li [2003] (dashed lines).

Figure 4. Compressional and shear-wave velocities projected to transition zone pressures at 300 K using finite-strain equations of state for hydrous Fe-bearing ringwoodite (this study, filled symbols and solid lines), anhydrous Fe-bearing ringwoodite [Sinogeikin *et al.*, 2003] (grey open symbols, grey solid lines) and anhydrous pure-Mg ringwoodite [Li, 2003] (black open squares, dashed lines).

Figure 5. Elastic anisotropy factor A (see text) for hydrous Fe-bearing ringwoodite (this study, filled circles, solid line), anhydrous Fe-bearing ringwoodite from *Sinogeikin et al.* [2003] (open diamonds, grey solid line) and for comparison MgO from *Sinogeikin and Bass* [2000] (open squares, dashed line).

Figure 6. Plot of the V_P/V_S ratio and Poisson's ratio for hydrous ringwoodite (this study, filled circles, solid lines), anhydrous ringwoodite from *Sinogeikin et al.* [2003] (open grey circles, grey solid lines), and anhydrous pure-Mg ringwoodite from *Li* [2003] (dashed lines). Hydration has a much larger effect of V_P/V_S than does Fe-content or temperature (not shown), and is the most diagnostic feature of hydrous ringwoodite.

Figure 7. Compressional and shear-wave velocities of ringwoodite projected along an adiabat (1673 K foot temperature) for anhydrous ringwoodite from *Sinogeikin et al.* [2003] (grey solid line) and hydrous ringwoodite (this study, solid black line) where dM/dT is assumed to be the same. The dashed line shows hydrous velocities when dM/dT is reduced by 15% (see text). Seismic models are PREM [*Dziewonski and Anderson*, 1981] and IASPEI91 [*Kennett and Engdahl*, 1991].

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Table 1. [100] P -velocities for hydrous Fo₉₀ ringwoodite.

P (GPa)	ρ (kg/m ³)	$V_P^{[100]}$ (m/s)	$\rho V^2 = C_{11}$ (GPa)
0	3651(5)	9036(62)	298(4)
1.15	3675	9182(82)	310(6)
2.36	3699	9256(62)	317(4)
3.71	3725	9428(45)	331(3)
4.65	3742	9524(46)	339(3)
5.48	3757	9576(54)	345(4)
6.28	3772	9661(60)	352(4)
7.04	3785	9720(68)	358(5)
7.71	3797	9771(59)	362(4)
8.50	3810	9834(57)	368(4)

Table 2. [100] S -velocities for hydrous Fo₉₀ ringwoodite.

P (GPa)	ρ (kg/m ³)	$V_S^{[100]}$ (m/s)	$\rho V^2 = C_{44}$ (GPa)
0	3651(5)	5536(20)	111.9(8)
2.32	3698	5585(20)	115.3(8)
2.98	3711	5591(24)	116.0(9)
3.48	3720	5606(12)	116.9(5)
4.17	3733	5620(21)	117.9(9)
4.81	3745	5635(10)	118.9(4)
5.92	3765	5652(13)	120.3(5)
6.60	3777	5669(19)	121.4(8)
7.16	3787	5679(12)	122.1(5)
7.75	3797	5685(23)	122.7(9)
8.37	3808	5691(19)	123.3(8)
9.00	3819	5703(17)	124.2(7)

Table 3. [110] P -velocities for hydrous Fo₉₀ ringwoodite.

Pressure (GPa)	ρ (kg/m ³)	$V_P^{[110]}$ (m/s)	$\rho V^2 =$ $\frac{1}{2}(C_{11}+2C_{44}+C_{12})$ (GPa)	C_{12}^* (GPa)
0	3651(5)	9334(70)	318(5)	113(2)
1.68	3685	9496(101)	332(7)	123(3)
2.84	3708	9593(66)	341(5)	128(2)
3.69	3724	9647(78)	347(6)	129(2)
5.65	3760	9783(54)	360(4)	134(1)
6.62	3778	9857(94)	367(7)	138(3)
7.39	3791	9938(96)	374(7)	144(3)
8.40	3808	10003(97)	381(7)	146(3)
9.20	3822	10061(99)	387(8)	149(3)

*calculated using V_P [110] and fits to C_{11} and C_{44} at these pressures.

Table 4. [111] S -velocities for hydrous Fo₉₀ ringwoodite.

Pressure (GPa)	ρ (kg/m ³)	$V_S^{[111]}$ (m/s)	$\rho V^2 =$ $\frac{1}{3}(C_{11}+C_{44}-C_{12})$ (GPa)	C_{12}^* (GPa)
0	3651(5)	5184(13)	98.1(5)	116.8(6)
1.8	3688	5254(15)	101.8(6)	123.2(7)
2.34	3698	5287(11)	103.4(4)	123.7(5)
3.06	3712	5324(15)	105.2(6)	125.1(7)
3.87	3728	5338(10)	106.2(4)	130.0(5)
4.40	3738	5373(12)	107.9(5)	130.1(6)
5.04	3749	5396(14)	109.2(6)	132.5(7)
5.64	3760	5413(11)	110.2(5)	135.2(6)
6.20	3770	5435(11)	111.4(5)	137.1(6)
6.59	3777	5445(14)	112.0(6)	138.9(7)
7.10	3786	5466(13)	113.1(6)	140.5(7)
7.68	3796	5484(16)	114.1(7)	143.0(8)

*calculated using $V_S^{[111]}$ and fits to C_{11} and C_{44} at these pressures.

Table 5. Single-crystal elastic properties of ringwoodite.

	X_{Fe}	H_2O (wt%)	C_{11} (GPa)	dC_{11}/dP	C_{44} (GPa)	dC_{44}/dP	C_{12} (GPa)	dC_{12}/dP	Ref.
<i>ringwoodite</i>									
$\gamma\text{-Mg}_2\text{SiO}_4$	0	0	327(3)		131(2)		114(2)		1
$\gamma\text{-Mg}_2\text{SiO}_4$	0	0	348	6.32	129	0.82	112	3.18	2
<i>hydrous ringwoodite</i>									
$\gamma\text{-Mg}_{1.89}\text{Si}_{0.97}\text{H}_{0.33}\text{O}_4$	0	2.2	281(6)		117(4)		92(5)		3
$\gamma\text{-Mg}_{1.85}\text{Si}_{0.985}\text{H}_{0.356}\text{O}_4$	0	2.3	290.6(7)		118.4(3)		104.0(6)		4
<i>Fo90 ringwoodite</i>									
$\gamma\text{-(Mg}_{0.91}\text{Fe}_{0.09})_2\text{SiO}_4$	0.09	0	329(2)	6.2(2)	130(2)	0.8(2)	118(3)	2.8(3)	5
<i>Fo90 hydrous ringwoodite</i>									
$\gamma\text{-(Mg}_{0.85}\text{Fe}_{0.11})_2\text{SiH}_{0.16}\text{O}_4$	0.11	1.0	299(4)	8.3(5)	112.2(5)	1.37(8)	116.2(4)	3.38(8)	6

¹[Jackson *et al.*, 2000]; Brillouin scattering, 1 atm.²[Kiefer *et al.*, 1997]; Pseudopotential calculation.³[Inoue *et al.*, 1998]; Brillouin Scattering, 1 atm.⁴[Wang *et al.*, 2003]; Brillouin Scattering, 1 atm.⁵[Sinogeikin *et al.*, 2003]; Brillouin Scattering (Pmax = 16 GPa).⁶This study. C_{ij} and C'_{ij} from fits to the experimental data (Pmax = 9 GPa).

Table 6. Aggregate elastic moduli and velocities of hydrous Fo₉₀ ringwoodite used for equation of state fitting.

Pressure* (GPa)	ρ (kg/m ³)	K_S (GPa)	G (GPa)	V_P (m/s)	V_S (m/s)	$\nu^\dagger$
0	3651(5)	177.1(20)	103.2(11)	9285(58)	5317(32)	0.256(3)
2.32	3698	188.8	107.7	9480	5396	0.260
2.98	3711	192.1	108.7	9531	5413	0.262
3.48	3720	194.6	109.8	9574	5433	0.263
4.17	3733	198.1	111.1	9630	5456	0.264
4.81	3745	201.3	112.4	9682	5478	0.265
5.92	3765	206.9	114.3	9768	5510	0.267
6.60	3777	210.3	115.7	9823	5534	0.268
7.16	3787	213.1	116.7	9867	5551	0.268
7.75	3797	216.0	177.7	9910	5567	0.270
8.37	3808	219.2	118.7	9955	5582	0.271
9.00	3819	222.3	119.8	10003	5602	0.272

Numbers in parenthesis represent one standard deviation in the last place. Uncertainties are estimated to be ~1% in aggregate moduli and ~0.5% in velocity, based upon uncertainties in C_{ij} .

*Pressures where C_{44} was determined directly. Precision is ~0.05 GPa from ruby fluorescence.

[†]Poisson's ratio.

Table 7. Thermoelastic properties of γ -(Mg,Fe)₂Si₂O₄.

	ρ_0 (kg/m ³)	V_P (km/s)	V_S (km/s)	K_{S0} (GPa)	$(dK_S/dP)_T$	$(dK_S/dT)_P$ GPa K ⁻¹	G_0 (GPa)	$(dG/dP)_T$	$(dG/dT)_P$ GPa K ⁻¹	Ref.
<i>ringwoodite</i>										
γ -Mg ₂ SiO ₄	3515(8)	9.86(3)	5.78(2)	185(2)	4.5(2)	-0.024(3)	120(1)	1.5(1)	-0.015(2)	[1,2]
<i>Fo90 ringwoodite</i>										
γ -(Mg _{0.91} Fe _{0.09}) ₂ SiO ₄	3701(5)	9.69(2)	5.68(1)	188(3)	4.1(3)	-0.021(2)	120(2)	1.3(2)	-0.016(2)	[3]
<i>Fo90 hydrous ringwoodite</i>										
γ -(Mg _{0.85} Fe _{0.11}) ₂ SiH _{0.16} O ₄	3651(5)	9.29(6)	5.32(3)	177(4)	5.3(4)		103.1(9)	2.0(2)		[4]

¹[Li, 2004]; Ultrasonic interferometry, Pmax = 12 GPa²[Jackson *et al.*, 2000]; Brillouin scattering, Tmax = 873 K³[Sinogeikin *et al.*, 2003]; Brillouin scattering, Pmax = 16 GPa, Tmax = 923 K⁴[Jacobsen *et al.*, 2004] and this study; GHz-ultrasonic interferometry, Pmax = 9 GPa

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Figure 7.