

Equation of state of hydrous Fo₉₀ ringwoodite to 45 GPa by synchrotron powder diffraction

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ABSTRACT

The equation of state of Fo₉₀ hydrous ringwoodite has been measured using X-ray powder diffraction to 45 GPa at the GSECARS beam line at the Advanced Photon Source synchrotron at Argonne National Laboratory. The sample was synthesized at 1400°C and 20 GPa in the 5000 ton multi anvil press at Bayerisches Geoinstitut in Bayreuth. The sample has the formula Mg_{1.70}Fe_{0.19}Fe_{0.02}²⁺Fe_{0.02}³⁺H_{0.13}-Si_{1.00}O₄ as determined by electron microprobe, Fourier transform infrared and Mössbauer spectroscopies, and contains ~0.79% H₂O by weight. Compression of the sample had been measured previously to 11 GPa by single crystal X-ray diffraction. A third-order Birch-Murnaghan equation of state fit to all of the data gives $V_0 = 530.49 \pm 0.07 \text{ \AA}^3$, $K_0 = 174.6 \pm 2.7 \text{ GPa}$ and $K' = 6.2 \pm 0.6$. The effect of 1% H incorporation in the structure on the bulk modulus is large and roughly equivalent to an increase in the temperature of ~600°C at low pressure. The large value of K' indicates significant stiffening of the sample with pressure so that the effect of hydration decreases with pressure.

KEYWORDS: equation of state, ringwoodite, synchrotron, Birch-Murnaghan equation.

Introduction

ALTHOUGH Earth's oceans cover >70% of the surface and liquid water completely dominates the surface processes of the planet, the oceans constitute only 0.025% of the planet's mass. In addition to controlling surface processes, water may also control the processes of the interior. Trace H in silicates controls their strength (Kavner, 2003), rheology and fracture properties (Karato, 1998) and can reduce the temperature of melt generation by hundreds of degrees C. The silicate rocks of the oceanic crust and lithospheric mantle may alter to stoichiometrically hydrous silicates such as serpentine, talc, amphibole, mica and lawsonite that are capable of incorporating an amount of water, principally as hydroxyl, roughly comparable to that of the liquid ocean. On subduction, most of these hydrous phases break

down and release their water to flux melting in the slab and overlying mantle wedge, so that most of this water is returned to the surface via arc volcanism (Schmidt and Poli, 1998; Dixon and Clague, 2001; White, 2002), or undersea serpentine mud volcanoes (Mottl *et al.*, 2003).

But is it all returned? Much of the water thought to be going down subduction zones is unaccounted for (Fischer *et al.*, 2002). Below 300 km depth, the nominally anhydrous silicates may play an increasingly important role in the water cycle of the planet. At pressures >10 GPa, olivine can incorporate 2000 ppm H₂O (Kohlstedt *et al.*, 1996) and perhaps as much as 8000 ppm in silica-deficient systems (Locke *et al.*, 2002). At depths of 410 to 525 km, wadsleyite (β -(Mg,Fe)₂SiO₄) can incorporate 3.3 wt.% H₂O (33,000 ppm) (Smyth 1987; 1994; Inoue *et al.*, 1998; Kohlstedt *et al.*, 1996). Ringwoodite (γ -(Mg,Fe)₂SiO₄) can incorporate at least 2.2 wt.% H₂O (Kohlstedt *et al.*, 1996; Kudoh *et al.*, 2000). If saturated, these nominally anhydrous silicates

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can incorporate many times the amount of water in the hydrosphere and may play a dominant role in the water cycle, exchanging with and maintaining ocean volume over geological time.

Ringwoodite is the spinel form of $(\text{Mg,Fe})_2\text{SiO}_4$ and is thought to constitute 50–80% of the mantle transition zone at depths of 525 to 660 km. It is nominally anhydrous, and compression measurements of anhydrous ringwoodite have been reported by Meng *et al.* (1993) and Zerr *et al.* (1993). Zerr *et al.* (1993) reported a bulk modulus of 183 ± 4 GPa for anhydrous, pure Mg ringwoodite. Hazen and Yang (1999) reviewed compression studies of spinel structures and calculated a bulk modulus of 187.2 GPa and assumed K' of 4 for an ordered Fo_{100} anhydrous composition. Elastic properties of anhydrous ringwoodite have been measured by Brillouin spectroscopy. Sinogeikin *et al.* (2001) gave an adiabatic bulk modulus of 188 ± 4.1 GPa and K' of 4 for anhydrous Fo_{89} ringwoodite, and a shear modulus of 120 ± 1.3 GPa.

In order to know if water is actually present in the solid silicate phases of the transition zone, it is necessary to know the elastic properties of ringwoodite as a function of H content as well as temperature and pressure. Smyth *et al.* (2003) reported crystal structures of seven samples of various H and Fe contents. They reported that the principal hydration mechanism involves octahedral cation vacancy charge-balanced by protonation and gave an estimated unit-cell volume of 560 \AA^3 for the hypothetical H_4SiO_4 spinel. Hydration has a first-order effect on the elastic properties of this material. Kudoh *et al.* (2000) report the crystal structure of hydrous ringwoodite and found both cation vacancies and cation disorder in Fe-free hydrous ringwoodite. Yusa *et al.* (2000) report a compression study giving a bulk modulus of 148 GPa for a pure Mg sample with 2.8 wt.% H_2O . Smyth *et al.* (2004) report a single-crystal compression study of a Fo_{89} -composition sample containing 0.8 wt.% H_2O to 11 GPa giving an isothermal bulk modulus of 169.0 ± 3.4 GPa with a K' of 7.9 ± 0.9 . This refined value of K' is unusually large for a structure with close-packed oxygens.

Jacobsen *et al.* (2004) report ambient-condition elastic constants of $c_{11} = 298 \pm 13$, $c_{44} = 112 \pm 6$, and $c_{12} = 115 \pm 6$ GPa from single-crystal ultrasonic measurements giving an adiabatic bulk modulus of 176 ± 7 GPa. These data indicate that hydration to 1 wt.% H_2O has an effect on the P-wave velocity equivalent to raising the temperature

by $\sim 600^\circ\text{C}$ and on shear velocity by 1000°C . This means that hydration may have a larger effect on seismic velocities than temperature within the uncertainties of each in the transition zone, so that tomographic images of this region of the mantle are more likely to reflect hydration than temperature.

The ultrasonic study by Jacobsen *et al.* (2004) was done at ambient conditions, and the single crystal compression study of Smyth *et al.* (2004) only went to 11 GPa. In order to test the large K' value reported by Smyth *et al.* (2004) and to better estimate the effect of pressure on velocities in the hydrous material, we have undertaken a room-temperature compression study of this material to well above the stability limit of ringwoodite using powder X-ray diffraction and the GSECARS beam line at the Advanced Photon Source (APS) Synchrotron.

Experimental methods

A single-crystal sample of the hydrous ringwoodite (# SZ0002; Smyth *et al.*, 2003) was crushed to a fine powder of $\sim 1\text{--}3 \mu\text{m}$ grain size and loaded in a four-pin piston-cylinder type diamond anvil cell with an anvil-culet size of $250 \mu\text{m}$. The sample has the formula $\text{Mg}_{1.70}\text{Fe}_{0.19}^{2+}\text{Fe}_{0.02}^{3+}\text{H}_{0.13}\text{Si}_{1.00}\text{O}_4$ as determined by electron microprobe, and Fourier transform infrared and Mössbauer spectroscopies, and contains ~ 0.79 wt.% H_2O (Smyth *et al.*, 2003). Two pressure-volume experiments were performed. In the first experiment, argon was used as the pressure medium with a rhenium gasket. In the second experiment a mixture of methanol-ethanol (4:1 ratio) was used as the pressure medium with stainless steel as gasket. In both cases, gaskets were pre-indented to $\sim 30 \mu\text{m}$ thickness and holes of $\sim 130 \mu\text{m}$ depth were drilled as the sample chamber. The angle-dispersive X-ray diffraction experiments were performed at the GeoSoilEnviroCARS beam line (13-BM-D) at Advanced Photon Source (APS) using a monochromatic X-ray beam energy of 37.44 keV (0.3311 \AA). The average exposure time was 5 min. The two-dimensional X-ray patterns were integrated using the program FIT2D (Hammersley *et al.*, 1996) to produce 2 θ -intensity profiles (Fig. 1). Pressure was measured from the calibrated wavelength of the R1 fluorescence lines of small ruby crystals included in the sample chamber. The cubic unit-cell parameter of ringwoodite was refined using the Rietveld program

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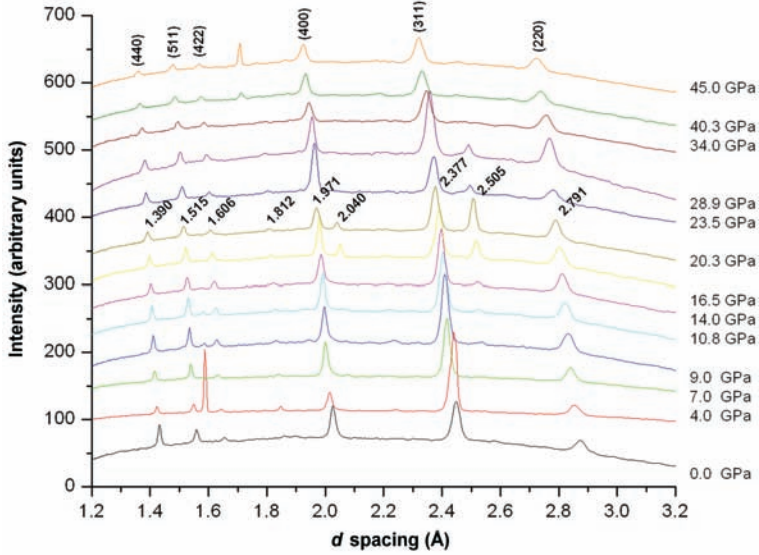


FIG. 1. Integrated synchrotron XRD patterns at all the pressures measured, methanol-ethanol pressure-medium.

GSAS (Larson and von Dreele, 2000) and reported in Table 1 along with relative cell volume V/V_0 . An example of the Rietveld fit profile is given in Fig. 2.

The preliminary unit-cell volume at zero pressure obtained in the synchrotron experiment is somewhat larger than that obtained by single-crystal diffraction. This may be due to a systematic error in the sample-to-detector distance in the synchrotron experiment, or less

likely, to a slight compositional gradient in the sample. To facilitate comparison of the two data sets and to compute the equation of state from the combined data sets we have used V/V_0 where V_0 is the zero-pressure volume obtained by each method. Plotting these relative unit-cell volume data together with the data of Smyth *et al.* (2004) we obtain the compression plot in Fig. 3. A plot of normalized pressure vs. Eulerian strain (F - f plot, Angel 2000) is given in Fig. 4.

Table 1. Unit-cell parameters of hydrous ringwoodite at various pressures in a pressure medium of ethanol-methanol.

Pressure (GPa)	a_{obs} (Å)	V_{obs} (Å ³)	V/V_0
0.0	8.1102(8)	533.45(15)	1.000
4.02	8.0520(24)	522.04(26)	0.9787(4)
7.04	8.0139(14)	514.67(13)	0.9648(2)
9.01	7.9905(9)	510.18(14)	0.9564(2)
10.79	7.9682(8)	505.91(14)	0.9484(3)
14.0	7.9476(8)	502.02(14)	0.9411(3)
16.5	7.9202(7)	496.83(17)	0.9314(3)
20.27	7.8811(11)	489.50(20)	0.9177(4)
23.50	7.8541(10)	484.49(21)	0.9083(4)
28.85	7.8206(7)	478.32(14)	0.8967(3)
34.04	7.7782(17)	470.58(20)	0.8822(4)
40.30	7.7285(12)	461.62(19)	0.8654(4)
45.0	7.6946(17)	455.57(22)	0.8541(4)

The program EOSFIT6.0 (Angel, 2000) was used to fit equation of state parameters to the observed compression data. We used a third-order Birch-Murnaghan formulation with an implied (and fixed) K'' (Angel, 2000). The powder diffraction unit-cell volumes from the ethanol-methanol experiment alone give a refined $K_0 = 183.1 \pm 5.0$, $K' = 6.0 \pm 0.4$, which yielded an implied value of $K'' = -0.06 \text{ GPa}^{-1}$. Combining these data with those of Smyth *et al.* (2004) we obtain a refined $K_0 = 171.8 \pm 2.7$, $K' = 7.1 \pm 0.4$, and $K'' = -0.06$ (fixed). The observations were weighted according to the estimated precision of the measurement, which does not include possible systematic error. The merged data set was fit using V/V_0 using separate V_0 values for the powder and single-crystal experiments. An estimated precision of 0.1 GPa in the ruby fluorescence pressure measurement was assumed. The pressure measurements used in the single-crystal data were obtained from unit-cell determinations of a quartz crystal standard

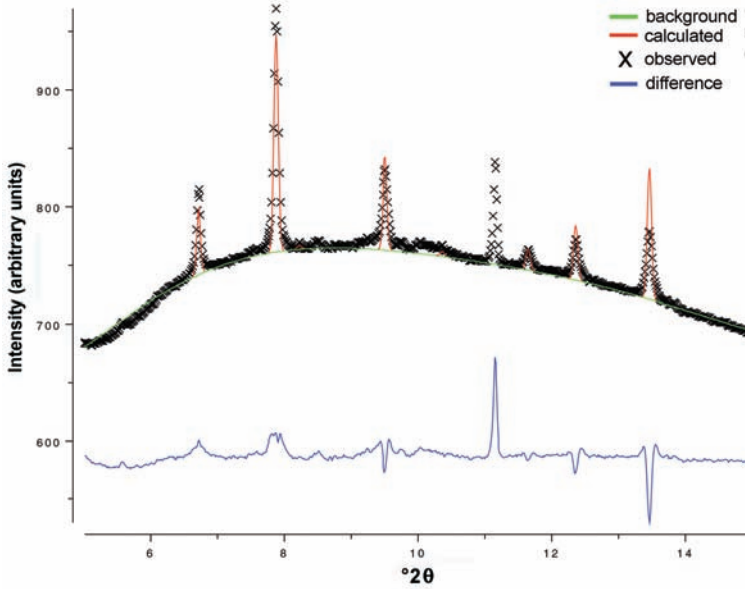


FIG. 2. Rietveld fit of ringwoodite powder diffraction pattern from program GSAS (Larson and von Dreele, 2000). The peak at 11.2° is from ruby. The calculated scattering intensities have not been corrected for diamond absorption which may account for the decrease in observed vs. calculated intensity with increasing scattering angle.

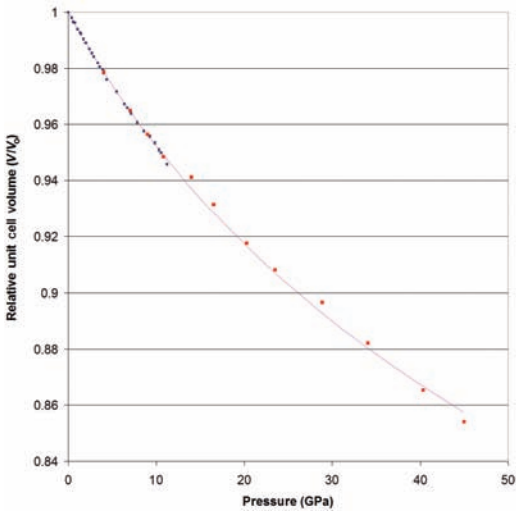


FIG. 3. Plot of relative unit-cell volumes (V/V_0) vs. pressure for hydrous Fo_{90} ringwoodite. The data from synchrotron powder diffraction (red symbols) extend the single-crystal data (blue symbols) pressure range by a factor of four. The curve is an equation of state of $K_0 = 171.8$; $K' = 7.1$. The internal precision of the unit-cell refinements is smaller than the symbol, though systematic errors, as discussed, may be larger.

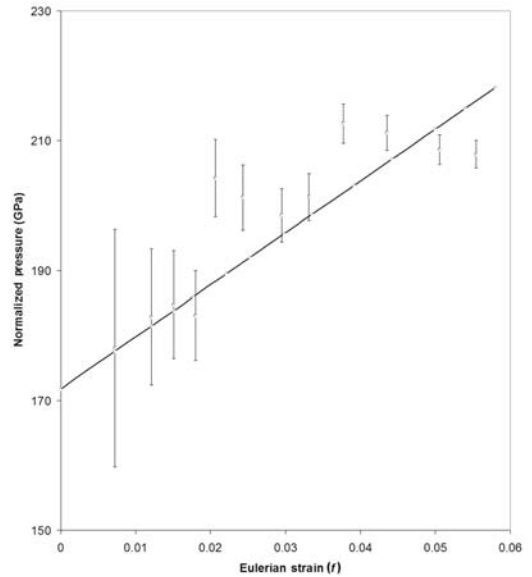


FIG. 4. Plot of normalized pressure vs. Eulerian strain (F - f plot, Angel, 2000) for the synchrotron compression data for hydrous ringwoodite. The curve is an equation of state of $K_0 = 171.8$; $K' = 7.1$. The error bars for normalized pressure assume a pressure error in the experiments of 0.4 GPa from ruby fluorescence. The plot shows a strong positive slope consistent with a $K' > 4.0$.

loaded together with ringwoodite in the diamond cell (Angel *et al.*, 1997). The pressure errors are the precision of the quartz cell volume determination (Smyth *et al.*, 2004).

Discussion

Smyth *et al.* (2004) obtained a bulk modulus of 169.0 ± 3.4 GPa with a K' of 7.9 ± 0.9 , based on single-crystal compression studies to 11 GPa. The current data give a bulk modulus of 183.0 ± 5.0 GPa with a K' of 6.0 ± 0.4 , but using only the data obtained to 30 GPa, the synchrotron data give a K_0 of 177 ± 7 GPa with a K' of 7.0 ± 0.9 , in very close agreement with the single-crystal data. The large K' values thus appear to be confirmed and are consistent with the hydration mechanism involving cation vacancies, which are likely to be highly compressible at low pressures but less so at higher pressure. Large values of K' are associated with structures such as micas containing large void spaces and large, compressible cations such as K^+ . In a single-crystal compression study, Smyth *et al.* (2000) observed a K' value of 9 for two polytypes of phengite mica. We have also obtained a bulk modulus of 146 GPa with K' of 6.1 in a single-crystal compression study of hydrous wadsleyite II (Smyth *et al.*, 2005).

Using the data of Smyth *et al.* (2003) we estimated the cell volume of anhydrous FO_{90} ringwoodite to be 529.65 \AA^3 compared to the hydrous value of 530.48 \AA^3 , resulting in a decrease in density of about 0.042 g/cm^3 . If we compare our refined equation of state parameters for hydrous FO_{90} ringwoodite to those of an anhydrous sample with a K_0 of 184 and a K' of 4 (assumed) (Hazen and Yang, 1999), we see that the cell volumes as a function of pressure do not cross but have a closest approach at ~ 6 GPa and diverge at higher pressures. This seems to indicate that the hydrous sample is less compressible at pressures above ~ 6 GPa. Given the initial volume expansion and reduction in formula weight with hydration, this would also imply significant buoyancy of the hydrous sample at transition zone pressures. Angel *et al.* (2001) reviewed the effects of hydration on elastic properties, and suggested that the softening observed with hydration in the dense hydrous magnesium silicate phases is more likely due to decreased density than simply to protonation. Also, as Angel *et al.* (2001) pointed out, we have few data on temperature effects on the bulk modulus for the

hydrous samples. Also it would be advisable to have compression data of comparable precision for the anhydrous material before firm conclusions on buoyancy can be drawn.

In Figs 3 and 4, a slight inflection of the compression curve is seen at ~ 30 GPa. Kleppe *et al.* (2002) noted a significant, reversible change in the Raman spectrum of this sample above 30 GPa. They suggested that the Raman peaks appearing in the $460\text{--}600 \text{ cm}^{-1}$ region may be the result of octahedral Si in the structure. It may be significant that the small inflection observed in the cell-volume data in this study is due to a reversible shift in coordination of Si. However, further studies will be required to confirm this observation. It should be noted that 30 GPa is well above the natural stability pressure of ringwoodite, which inverts to perovskite plus periclase at ~ 22 GPa at 1400°C . This reaction has been reported to have a slightly negative Clapeyron slope, so the reaction would probably occur at higher pressure at room temperature. It is possible therefore that the inflection observed in the data may be due to a metastable increase in coordination of Si. A slight increase in compressibility above 30 GPa is consistent with such a metastable intermediary phase (e.g. Smyth and Ahrens, 1997).

It is also possible that the inflection observed is due to non-hydrostatic pressure in the cell. The pressure medium is ethanol-methanol which is known to form a stiff, amorphous solid at pressures >25 GPa. We also conducted a compression experiment in Ar, but the pressure medium was contaminated with N_2 , and both the Ar and N_2 form crystalline solids at pressures >1 GPa. The presence of N_2 , which has a complex polymorphism in this pressure range, rendered the powder diffraction patterns too complex for unambiguous unit-cell refinements of the ringwoodite.

In summary, we have obtained room-temperature compression data to 45 GPa using powder diffraction of synchrotron radiation at the GSECARS beam line at APS on a sample of hydrous ringwoodite. The refined compression parameters from the powder data alone are K_0 of 183.0 ± 5.0 GPa with a K' of 6.0 ± 0.4 . When these data are combined with single-crystal compression data obtained on the same sample, the refined compression parameters are $V_0 = 530.49 \pm 0.07 \text{ \AA}^3$, $K_0 = 171.8 \pm 2.8$ GPa and $K' = 7.1 \pm 0.4$. The decrease in K and increase in K' relative to anhydrous ringwoodite observed in the previous

study are confirmed. The unusually large K' value for a close-packed oxygen structure may be the result of compressing relatively large and compressible octahedral cation vacancies that result from hydration.

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