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 formula $\text{Mg}_{1.70}\text{Fe}^{2+}_{0.19}\text{Fe}^{3+}_{0.02}\text{H}_{0.13}\text{Si}_{1.00}\text{O}_4$ as determined by electron microprobe, FTIR and Mössbauer spectroscopy and contains approximately 0.79 percent H₂O by weight. Compression of the sample had been previously been measured 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 one percent H incorporation in the structure on the bulk modulus is large and roughly equivalent to an increase in the temperature by about 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.

Introduction

Although Earth's oceans cover more than seventy percent of the surface and liquid water completely dominates the surface processes of the planet, the oceans constitute only 0.025 percent 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 Celcius. 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 above 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 weight percent 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 percent by weight H₂O (Kohlstedt et al., 1996, Kudoh et al., 2000). If saturated, these nominally anhydrous silicates 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 geologic time.

Ringwoodite is the spinel form of (Mg,Fe)₂SiO₄ and is thought to compose 50 to 80 percent 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) report a bulk modulus of 183 ± 4 GPa for anhydrous, pure Mg ringwoodite. Hazen and Yang (1999) reviewed compression studies of spinel structures and calculate a bulk modulus of 187.2 GPa and assumed K' of 4 for an ordered Fo₁₀₀ anhydrous composition. Elastic properties of anhydrous ringwoodite have been measured by Brillouin spectroscopy. Sinogeikin et al. (2001) give an adiabatic bulk modulus of 188 ± 4.1 GPa and K' of 4 for anhydrous Fo₈₉ 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) report crystal structures of seven samples of various H and Fe contents. They report that the principal hydration mechanism involves octahedral cation vacancy charge-balanced by protonation and give an estimated unit cell volume

of $560 \text{ \AA}^3$ 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 weight percent H_2O . Smyth et al (2004) report a single-crystal compression study of a Fo_{89} -composition sample containing 0.8 weight percent 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 one percent by weight H_2O has an effect on the P-wave velocity equivalent to raising the temperature by about 600°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 about 1-3 μm grain size and loaded in a four-pin piston-cylinder type diamond anvil cell with an anvil-culet size of 250 μm . The sample has formula $\text{Mg}_{1.70}\text{Fe}^{2+}_{0.19}\text{Fe}^{3+}_{0.02}\text{H}_{0.13}\text{Si}_{1.00}\text{O}_4$ as determined by electron microprobe, FTIR and Mössbauer spectroscopy and contains approximately 0.79 percent H_2O by weight (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 about 30 μm thickness and holes of about 130 μm 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 29.2 KeV (0.3311 $\text{\AA}$). The average exposure time was 5 minutes. The two-dimensional X-ray patterns were integrated using the program FIT2D (Hammersley et al., 1996) to produce two-theta-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 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 Figure 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 is most likely a systematic error in the sample to detector distance in the synchrotron experiment. 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 Figure 3. A plot of normalized pressure versus Eulerian strain (F - f plot, Angel 2000) is given in Figure 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 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) to estimate the cell volume of anhydrous Fe_{90} ringwoodite to be $529.65 \text{ \AA}^3$ compared to the hydrous value of $530.48 \text{ \AA}^3$, resulting in a decrease in density of about 0.042 g/cm^3 . If we compare our refined equation of state parameters for hydrous Fe_{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 about 6 GPa and diverge at higher pressures. This seems to indicate that the hydrous sample is less compressible at pressures above about 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) have reviewed the effects of hydration on elastic properties, and suggest 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) point out, we have little data on temperature effects on 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 Figures 3 and 4, a slight inflection of the compression curve is seen at about 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 region 460 to 600 cm^{-1} may be the result of octahedral silicon 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 about 22 GPa at 1400 °C. This reaction has been reported to have a slightly negative Clapeyron slope, so the reaction would likely 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 silicon. 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 above 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 above about 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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Table 1. Unit Cell Parameters of Hydrous Ringwoodite at various pressures in a pressure medium of ethanol-methanol.

Pressure (GPa)	$a_{\text{obs}}(\text{\AA})$	$V_{\text{obs}}(\text{\AA}^3)$	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)

Figure 1: Integrated synchrotron X-ray diffraction patterns at all the pressures measured, methanol-ethanol pressure-medium

Figure 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 from diamond absorption which may account for the decrease in observed versus calculated intensity with increasing scattering angle.

Figure 3. Plot of relative unit cell volumes (V/V_0) versus pressure for hydrous Fo₉₀ ringwoodite. The data from synchrotron powder diffraction (red symbol) extend the single-crystal data (small symbol) 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, however systematic errors, as discussed, may be larger.

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Figure 4. Plot of normalized pressure versus 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 $K' > 4.0$.