Compressibility and structural stability of two variably hydrated olivine samples (Fo$_{97}$Fa$_3$) to 34 GPa by X-Ray diffraction and Raman spectroscopy

Murli H. Manghnani, Anwar Hushur, Joseph R. Smyth, Fabrizio Nestola, Przemyslaw Dera, Mariappan Sekar, George Amulele, Daniel J. Frost

1University of Hawaii, Hawaii Institute of Geophysics and Planetology, Honolulu, HI 96822, USA (murli@soest.hawaii.edu)

2Present address: School of Physics Science and Technology, Xinjiang University, Urumqi, 830046, P. R. China

3Department of Geological Sciences, University of Colorado, Boulder, CO 80309, USA

4Department of Geosciences, University of Padova, Via Gradenigo 6, I-35131, Padova, Italy

5Center for Advanced Radiation Sources, The University of Chicago, Argonne National Laboratory

6Present address: Indira Gandhi Center for Atomic Research, Kalpakkam 603 102, Tamil Nadu, India

7Present address: Department of Geology and Geophysics, Yale University, New Haven CT 06520, USA

8Bayerisches Geoinstitut, Universität Bayreuth, 95440, Bayreuth, Germany
ABSTRACT

Two hydrous olivines of composition Fo97Fa3 with water content of 4883 parts per million by weight (ppmw) (SZ0407A) and 8000 ppmw (SZ0407B) were synthesized at 1250 ºC and 12 GPa. Single-crystal X-ray diffraction was used to determine unit cell parameters of SZ0407A and SZ0407B at pressures up to 7.1 GPa at room temperature. Synchrotron powder X-ray diffraction and Raman scattering experiments were performed on sample SZ0407A in a diamond-anvil cell to 34 GPa at room temperature. For both samples, the compressibility is the largest along the b-axis and smallest along the a-axis. Using the compression $(V/V_0)$ vs. pressure data for sample SZ0407A to 29.08 GPa, in conjunction with the third-order Birch-Murnaghan equation of state, we calculate the isothermal bulk modulus and its pressure derivative as $K_o = 119.4(15)$ GPa and $K_o' = 6.6(5)$. Single-crystal compression data for sample SZ0407A to 7 GPa give $K_o = 121.5(6)$ GPa and $K_o' = 5.7(2)$; and for sample SZ0407B $K_o = 122.2(12)$ GPa and $K_o' = 6.2(4)$. High-pressure Raman spectra for SZ0407A up to 34 GPa show a continuous shift of all the observed bands to higher frequency with increasing pressure; there is no indication of any first-order phase transition. However, the Raman spectra indicate subtle discontinuous changes around 22 GPa, unobserved in previously reported studies on anhydrous olivines.

Keywords: Hydrous olivine, X-ray diffraction, Raman spectroscopy, hydration mechanism, high pressure
INTRODUCTION

The nominally anhydrous mineral phases in the Earth’s deep upper mantle and transition zone (410-660 km depth) may serve as a large internal reservoir of water that has profound implications for Earth’s evolution as a water planet. Water plays important roles in the phase transformation kinetics in the Earth’s interior, which affects the mantle dynamics (e.g. Kubo et al. 1998). Trace or minor hydroxyl in these phases affects strength and rheology (Chen et al. 1998; Kavner 2003; Mei and Kohlstedt 2000), and electrical conductivity (Poe et al. 2010). Therefore, it is important to understand the state of water and its role in the structure of minerals in the Earth’s interior. Much effort has been put into estimating the OH⁻ storage capacity of nominally anhydrous mineral phases to determine factors controlling OH⁻ incorporation into the structure (Bai and Kohlstedt 1993; Bell et al. 2003; Hushur et al. 2009; Khisina et al. 2001; Kohlstedt et al. 1996; Mackwell and Kohlstedt 1990; Matveev et al. 2001; Miller et al. 1987; Mosenfelder et al. 2006; Rossman and Smyth 1990; Skogby et al. 1990; Smyth 1994; Walker et al. 2007). These studies have revealed that hydroxyl occurrence in nominally anhydrous mantle phases is closely related to cation vacancy defects. Although point defects have been linked to hydrogen incorporation, there remain several questions as to which point defect predominates under various $P,T$ conditions.

Olivine $(\text{Mg,Fe})_2\text{SiO}_4$ is the most abundant mineral phase in the upper mantle to a depth of 410 km, and it is nominally anhydrous. Although natural olivines typically contain less than 200 ppmw $\text{H}_2\text{O}$ by weight, samples synthesized at pressures of 12-14 GPa have been obtained with up to 8900 ppmw, enough to significantly affect elastic and other physical properties (Litasov et al. 2007; Smyth and Jacobsen 2006) as well as the overall hydrogen budget of the planet. This has generated broad interest in systematic investigation of the various structural and elastic (seismic) properties, as well as the stability of these phases as a function of water content. X-ray diffraction (XRD) can give the full image of a crystal structure averaged over a sample volume; however information on local structural disorder,
dynamics and defects with small concentrations may be limited. In contrast, spectroscopy is very sensitive to the local structural disorder and defects. A combination of both XRD and spectroscopic studies may give important additional information on crystal structures such as disorder and dynamics, and may even help avoiding pitfalls in structure solution (Libowitzky 2006).

The XRD technique has been applied in various previous studies to understand the structure and compressibility of both hydrous and anhydrous olivines. Isothermal compression methods, deploying powder or single-crystal X-ray diffraction techniques, yield unit cell volume as a function of pressure ($P$-$V$ relations) which enables calculation of isothermal bulk modulus ($K_T$) and its pressure derivative ($\partial K_T/\partial P$). The isothermal bulk modulus $K_T$ is related to the adiabatic bulk modulus $K_s$ by

$$K_s = K_T (1 + \alpha \gamma T),$$

where $\alpha$ is the thermal expansion coefficient (~2.6 x 10^{-5} K^{-1}) (Fei 1995; Kroll et al. 2012; Ye et al. 2009), $\gamma$ is the Grüneisen parameter (~1) (Anderson 1989), and $T$ is temperature (K). In general, $K_s$ is roughly one to two percent larger than $K_T$. Table 1 summarizes elasticity data for anhydrous and hydrous olivines. One of the major findings is that the effect of hydration is to decrease bulk modulus ($K_o$) and increase $K_o'$ by increasing the vacancy or unoccupied volume in the structure.

Anhydrous olivine has been widely studied by vibrational spectroscopies. The pressure dependencies of the Raman and IR spectra at room temperature have been measured in several studies for the end-members forsterite and fayalite, as well as for some intermediate compositions. Both Raman (Besson et al. 1982; Chopelas 1990; Durben et al. 1993; Gillet et al. 1991; Wang et al. 1993) and IR data (Hofmeister 1997; Hofmeister et al. 1989; Williams et al. 1990) show that the high frequency modes (> 500 cm^{-1}), related to the internal vibrations of the isolated SiO$_4$ tetrahedra of the olivine structure have smaller mode Grüneisen parameters than the lattice modes, which involve vibrations of the MgO$_6$ octahedra. This effect is consistent with the larger compressibility and relative weakness of the Mg-O bond compared to the Si-O bond as shown by high pressure x-ray diffraction studies (Hazen 1976; Kudoh and Takéuchi 1985), and discussed in detail by Smyth et al. (2000). Vibrational studies to date have not been carried out for Fe-bearing olivines with significant hydration. We report...
here single-crystal XRD data up to 7.1 GPa, powder synchrotron XRD data up to ~29 GPa, and Raman spectroscopic data of synthesized hydrous Fo$_{97}$Fa$_3$ olivine samples in the diamond anvil cell up to 34 GPa. Raman spectra of high-quality single crystals of hydrous olivine were measured in the wide spectral range of 190 – 3700 cm$^{-1}$. Our aim was to investigate the effect of water on the compressibility and vibrational properties, the local structure of hydrous Fe-bearing olivine, and to track changes in H bonding and proton environments under pressure.

**EXPERIMENTAL METHODS**

Synthesis of these hydrous olivines was carried out in double-capsule experiments in the 5000-ton multi-anvil press at Bayerisches Geoinstitut at 12 GPa and 1250°C (Smyth et al. 2006). In these experiments, pyroxene-normative and periclase-normative compositions were formulated with about 3 weight percent H$_2$O. The two compositions were welded into separate inner Pt capsules and packed with brucite into a welded outer capsule. When the inner capsules were opened free liquid water emerged. The silica-excess capsule contained olivine, enstatite, and a small amount of apparent quench melt phase. The silica deficient capsule contained olivine, clinohumite and a quenched melt phase. The olivine, clinohumite and clinoenstatite were identified by Raman spectroscopy and by single crystal X-ray diffraction. The grain size of the silica excess sample was about 100 μm, whereas that of the silica deficient capsule was about 250 μm. H$_2$O contents were measured by polarized FTIR spectroscopy on X-ray-oriented, faceted single crystals. The contents were computed from integrated absorbances using the calibration of Bell et al. (2003) for olivine. Sample SZ0407A contained 4883 (±500) ppmw H$_2$O, whereas sample SZ0407B contained 8000 (±500) ppmw.

Unit-cell parameters were measured as a function of pressure up to 7.1 GPa by single-crystal X-ray diffraction. For the single crystal X-ray diffraction we used a steel gasket T-301 and methanol:ethanol 4:1 mixture was used as transmitting pressure, which is hydrostatic at least up to 9.4 GPa as demonstrated by Angel et al. (2007). The X-ray source was the MoKalpha with working conditions at 50 kV and 40 mA. Two crystals (SZ0407A and B) were loaded into the diamond cell along with a quartz crystal for an internal pressure standard. Cell parameters of the two crystals and quartz were measured at 13 different pressures up to 7.1 GPa using a Huber four-circle
diffractometer operating under the program SINGLE (Angel and Finger 2011). Pressures were determined using the quartz calibration curve of Angel et al. (1997).

High-pressure synchrotron powder X-ray diffraction studies in angle-dispersive mode on the hydrous olivine (SZ0407A) were carried out up to 29 GPa at the GeoSoilEnviroCARS beam line (13-BM-D) at the Advanced Photon Source (APS) using a monochromatic X-ray beam of energy of 37.07 keV ($\lambda = 0.3344 \, \text{Å}$). Finely powdered samples of grain size 1-3 μm were loaded in a piston-cylinder type diamond-anvil cell (DAC) of culet size 250 μm. We used a steel gasket T-301 and silicone oil was used as the pressure transmitting medium. The pressure was estimated using the shift in the R1 line of the ruby loaded along with the sample (Mao et al. 1986). The average time for measurement at each pressure was 10 minutes. Fit2D (Hammersley et al. 1996) was used to reduce the data to 2-theta vs. intensity profiles. The unit-cell parameters were estimated from the d-spacings at each pressure using the program Unit Cell (Holland and Redfern 1997). We have used the peaks (1 1 2), (1 3 0), (1 0 2), (0 2 1) and (0 2 0) for the lattice parameter calculation.

Raman spectra were recorded using a triple monochromator Dilor XY spectrometer equipped with a liquid nitrogen-cooled charge-coupled-device (CCD) detector. The 514.5 nm green line of an Ar ion laser from Spectra Physics was used to excite the sample. The laser light was focused using an OLYMPUS microscope with a long distance 50× objective to a spot of about 3 μm diameter in the sample with the laser power being 25 mW on the sample. No laser heating effects should occur under such conditions. The spectrometer was calibrated using single-crystal silicon as a reference. For high-pressure measurements in the diamond anvil cell, a rhenium gasket was pre-indentented to 42 μm thickness and an 85 μm diameter hole was drilled at the center of the indentation. A randomly oriented single crystal fragment $35 \times 40 \times 20 \, \mu m^3$ in size was mounted in a diamond-anvil cell where diamonds had 350 μm diameter culets. Two pieces of ruby ~5 μm in size were placed at the two sides of the sample for pressure calibration. Liquid argon was loaded as a pressure-transmitting medium using a liquid nitrogen cooling method. Pressure was estimated using the shift in the R1 line of the ruby loaded along with the sample (Mao et al. 1986). All spectra were recorded in the backscattering geometry with no polarization used for the collected signal.
RESULTS AND DISCUSSION

Unit cell parameters of hydrous Fo$_{97}$ containing 4883 ppmw H$_2$O (SZ0407A) and hydrous Fo$_{97}$ containing 8000 ppmw H$_2$O (SZ0407B) measured at ambient conditions and 12 pressures by single-crystal XRD are reported in Table 2. The measured pressure dependencies of the unit-cell volumes are plotted in Figures 1 and 2. The program EOSFIT5.2 (Angel 2002) was used to fit equation of state parameters to the observed compression data. The fitting is weighted according to the estimated error of pressure determination and fitting error of volume determination. The isothermal bulk modulus and its derivative were estimated using the third order Birch-Murnaghan equation of state.

\[
P(V) = \frac{3K_o}{2} \left[ \left( \frac{V_o}{V} \right)^3 - \left( \frac{V_o}{V} \right)^5 \right] \left[ 1 + \frac{3}{4} (K'_o - 4) \left( \frac{V_o}{V} \right)^3 - 1 \right]
\]

where $K_o$ is the bulk modulus at ambient pressure, $K'_o$ is its first pressure derivative, and $V_o$ is the reference volume. Single crystal data to 7.1 GPa give $K_o = 121.5(6)$ GPa and $K'_o = 5.7(2)$ for sample SZ0407A, and $K_o = 122.2(12)$ GPa and $K'_o = 6.2(4)$ for sample SZ0407B. The $K_o$ and $K'_o$ of SZ0407A and SZ0407B show that slightly different water content (~3200 ppmw) has minimal effect on the bulk modulus within experimental uncertainty. The values are $K_o = 119.2(12)$ GPa and $K'_o = 6.6(0.4)$ for combined single-crystal and powder diffraction data for sample SZ0407A, and no distinctive changes were observed in the isothermal volume compressibility. The compression data for all samples are thus in very good agreement and indicate a decrease of about 6 percent in bulk modulus relative to anhydrous forsterite data cited above. Comparison of bulk modulus of hydrous Fo$_{97}$ containing 8000 ppmw H$_2$O with hydrous Fo$_{95}$ containing 8000 ppmw H$_2$O (Smyth et al. 2005; Smyth and Jacobsen 2006) which is 120(2) GPa shows that the 2 mol% Fe has no effect on $K_o$ within experimental uncertainty. Although we observe a decrease in bulk modulus with hydration, the effects of hydration on elasticity of forsterite may not be simple. Mao et al. (2010) report a crossover of the velocities of hydrous and anhydrous forsterite measured by Brillouin scattering at high pressure.
The axial compressibility is the largest along the $b$ axis and smallest along the $a$ axis as shown in Figure 3. The axial compression values were $\beta_a = 0.00166(2)$, $\beta_b = 0.00309(4)$, and $\beta_c = 0.00243(3)$ GPa$^{-1}$ for SZ0407A, respectively. For SZ0407B, the axial compression values were $\beta_a = 0.00158(3)$, $\beta_b = 0.00308(4)$, and $\beta_c = 0.00240(3)$ GPa$^{-1}$. The $a:b:c$ axial compressibility ratio was 1:1.9:1.5 for both SZ0407A and SZ0407B. The anisotropic nature of the compression is a common feature for all anhydrous olivines. The compression along the $b$ axis depends on the compression of the most compressible structural unit, the M2 octahedron.

Our result is consistent with studies on anhydrous olivines, with the $b$ axis being the most compressible axis. However, our results also indicate an increase of the compressibility along the $a$ and $c$ axis as compared to the anhydrous forsterite and anhydrous olivine Fo$_{83}$Fa$_{17}$ (Andrault et al. 1995; Smyth et al. 2000; and references therein), which may be related to the hydration mechanism in hydrous olivine (SZ0407A, SZ0407B).

Raman spectra in the lattice and silicate vibrational region of hydrous olivine Fo$_{97}$Fa$_3$ containing 4883 ppmw water (SZ0407A) measured as a function of pressure to 34 GPa are shown in Figure 4. The ambient spectra are similar to those reported in previous Raman studies (Besson et al. 1982; Chopelas 1990, 1991; Durben et al. 1993; Gillet et al. 1991; Iishi 1978; Piriou and McMillan 1983; Wang et al. 1993). With increasing pressure, all the twelve observed modes show a continuous shift to higher frequency. Of these, four modes exhibit a linear pressure dependence of frequency; however the remaining eight modes are characterized by a nonlinear response. For these 8 modes, the frequency vs. pressure data were fitted with quadratic equations as shown in Figures 5 and 6. According to the original definition for a vibrational mode of frequency $\nu_i$, a mode Grüneisen parameter is defined by

$$\gamma_i = -\frac{d \ln(\nu_i)}{d \ln(V)}$$

where $V$ is volume. $\gamma_i$ were determined by fitting $\ln(\nu_i)$ versus $\ln(V)$ values linearly, and are shown in Table 3. $\gamma_i$ of the mode related to Mg(2)O$_6$ translation (Table 3) does not show marked changes in hydrous olivine Fo$_{97}$Fa$_3$ (SZ0407A) relative to anhydrous forsterite. $\gamma_i$ of all the observed modes related to SiO$_4$ tetrahedra show an increase as compared to those for anhydrous forsterite, indicating Si-O bonds in hydrous olivine Fo$_{97}$Fa$_3$ (SZ0407A) are more compressible than Si-O bonds in anhydrous olivine. This may be responsible for the increase of the compressibility along the $a$ and $c$ axis as compared to the anhydrous forsterite and...
anhydrous olivine Fo$_{83}$Fa$_{17}$ (Andrault et al. 1995; Smyth et al. 2000; and references therein).

Our Raman study on Fe-free hydrous forsterite does not show such an increase in $\gamma_i$ of the modes related to SiO$_4$ tetrahedra (Hushur et al. 2009), which may indicate that the hydration mechanism is different in hydrous olivine Fo$_{97}$Fa$_3$ (SZ0407A) as compared to the hydrous forsterite. May be, a significant protonation of Si-vacancies also exist in this hydrous olivine Fo$_{97}$Fa$_3$.

In the entire pressure range of this study, the sharp Raman bands assigned to vibrations of the olivine crystal structure are retained, indicating no evidence of any phase transition. However, the high-pressure spectra do indicate some subtle structural modification. Specifically, in the low frequency spectra range between 200 cm$^{-1}$ and 800 cm$^{-1}$, the M2 translation mode at 302.5 cm$^{-1}$, SiO$_4$ rotation mode at 325.2 cm$^{-1}$ and $\nu_4$ mode at 542.3 cm$^{-1}$ disappears, whereas the $\nu_4$ mode at 606.9 cm$^{-1}$ intensifies in the high pressure Raman spectra as shown in Figure 5. Both 542.3 cm$^{-1}$ and 606.9 cm$^{-1}$ modes are initially $A_g$ modes and represent anti-symmetric bending of the oxygens in SiO$_4$ tetrahedra. The disappearance of the 542.3 cm$^{-1}$ mode above 22 GPa, while the mode at 606.9 cm$^{-1}$ is intensified, is not an effect of sample orientation. This may indicate that the two bands represent vibrations of different structural units that appear or disappear above 22 GPa. Interestingly, the similarity of the high-pressure spectra with those of $\gamma$-spinel becomes more pronounced at high pressures: an intense band with a zero pressure location near 600 cm$^{-1}$, and a doublet at higher frequencies (Chopelas et al. 1994; Kleppe et al. 2002). The decrease in number of the Raman active modes at high pressure may indicate that the olivine structure is modified locally above 22 GPa, with the partial appearance of Si-O-Si linkages accompanied by a possible metastable increase in the silicon coordination. In our recent Raman study on Fe-free hydrous forsterite we observed a change in the pressure derivatives of many of the observed Raman modes at ~20 GPa (Hushur et al. 2009). However, in the current study on Fe-bearing hydrous forsterite we do not observe such a slope change at ~20 GPa. This may be related to different local environments in Fe-bearing hydrous forsterite as compared to the Fe-free hydrous forsterite.

The olivine structure is orthorhombic containing isolated SiO$_4$ units linked by octahedrally coordinated divalent cations. The divalent cations are in two crystallographically distinct sites, the smaller M1 ($C_i$ symmetry) site and larger M2 ($C_s$ symmetry) site. The M1 octahedron shares six edges with neighboring polyhedra, two with SiO$_4$ tetrahedra. The M2
octahedra share three edges with neighboring polyhedra but only one with a SiO$_4$ tetrahedron. The unit cell parameters increase in Fe-bearing hydrous forsterite as compared to the Fe-free hydrous forsterite that has the same amount of hydrogen present. Kudoh et al. (2006) and Kudoh et al. (2007) reported on a single-crystal X-ray structural analysis of Fe-bearing (Mg$_{1.85}$Fe$_{0.14}$Si$_{0.99}$H$_{0.06}$O$_4$) and Fe-Free (Mg$_{1.985}$Si$_{0.993}$H$_{0.06}$O$_4$) hydrous forsterite, in which increases in the $a$, $b$, and $c$ axes due to the effect of Fe were 0.13%, 0.08%, and 0.03%, respectively, and showing a 0.2% increase in the unit cell volume due to the presence of Fe. In Fe-bearing hydrous forsterite, cation vacancies predominantly occurred at the M2 site (Kudoh 2008; Kudoh et al. 2007), in contrast to the case of Fe-free hydrous forsterite in which the cation vacancies predominantly occur at the M1 site (Hushur et al. 2009; Kudoh 2008; Kudoh et al. 2006; Smyth et al. 2006). A vacancy at the M1 site leads to an increase in the M2-O bond length in Fe-free hydrous forsterite. In case of the Fe-bearing hydrous forsterite, Fe atoms lead to an increase in both the M1-O and M2-O bond lengths. The difference in proton occupancy between Fe-bearing hydrous forsterite and the Fe-free hydrous forsterite may be responsible for the different pressure dependence of the Raman modes observed in the Fe-bearing hydrous forsterite as compared to the Fe-free hydrous forsterite.

The Raman modes of the hydroxyl groups in hydrous olivine (SZ0407A) are shown in Figure 7. We fit the observed spectra at ambient pressure by four Gaussian functions using ORIGIN Pro 7.5 software. The spectra above 9 GPa are fitted with three Gaussian functions. The mode frequency as a function of pressure obtained by fitting is shown in Figure 8. At ambient pressure, four Raman bands were observed at 3555, 3578, 3613, and 3656 cm$^{-1}$. It is similar to the FTIR spectra measured on the sample SZ0407B and SZ0408A (Smyth et al. 2006), and Raman spectra of the sample SZ408A (Hushur et al. 2009). However, an additional Raman mode at 3656 cm$^{-1}$ is observed only on this hydrous olivine (SZ407A). As pressure increases, the Raman active OH stretching modes of hydrous olivine (SZ0407A) with frequencies < 3600 cm$^{-1}$ have strong, negative pressure dependence whereas OH modes at higher frequencies are less sensitive to pressure. According to the empirical relation between OH-stretching frequencies and O···O distances (Libowitzky 1999), a negative frequency response of OH modes under pressure requires a reduction of the respective O···O distances and indicates a strengthening of the hydrogen bond.
The protonation of hydrous olivine has been studied extensively by FTIR spectroscopy. Previous studies show that there are two different mechanisms related to silicon and magnesium vacancies by which hydrogen is incorporated into olivine crystal structure. Bai and Kohlstedt (1993) and Kohlstedt et al. (1996) suggested protonation of Mg-vacancies in the olivine structure, whereas Litasov et al. (2009), Matveev et al. (2001) and Lemaire et al. (2004) preferred significant protonation of Si-vacancies. Assuming linear O-H…O topologies, we can correlate the observed OH stretching frequencies with O…O bond distances (Libowitzky 1999). Octahedral edges in the olivine structure range from 2.85 to 3.33 Å except for edges shared with the tetrahedron, which are about 2.55 Å. Tetrahedral edges range from 2.55 to 2.76 Å. The largest and broad peak in the pattern at 3555 cm\(^{-1}\) (in the \(b\)-direction) is consistent with protonation of the shared O3-O3 edges (2.76 Å) of the M2 octahedron. The mode at 3578 cm\(^{-1}\) could correspond to the unshared O1-O3 edge of M1 (2.84 Å). The peak at 3613 cm\(^{-1}\) corresponds to protonation of an O-O distance of > 2.8 Å (Libowitzky 1999), and is consistent with the O1-O2 edge shared between M1 octahedra (2.85 Å). There is also the possibility of the O3-O3 edge of the M2 octahedron (2.99 Å), but a proton on this edge would require a strongly bent O-H…O angle to be consistent with polarizations. The mode at 3656 cm\(^{-1}\) corresponds to protonation of an O-O distance of > 2.9 Å (Libowitzky 1999) and is consistent with the O3-O3 edge of the M2 octahedron (2.99 Å) in this Fe-bearing olivine. There might be significant deviations from the linear O-H…O topologies, or the stretching mode at 3656 cm\(^{-1}\) is not from the hydrogen bonded O-H group. Khisina et al. (2001) reported an OH band at 3656 cm\(^{-1}\) which is related to the 10 Angstrom phase. However the strong intensity of this band in our spectra indicates that it is not from the minor phases in olivine. And also the single crystal data of our synthetic sample did not show any monoclinic phase in our studied sample. Therefore, it is not likely from the 10 Angstrom phase. May be the band at 3656 cm\(^{-1}\) is related to the Si vacancies. The band at 3656 cm\(^{-1}\) shows splitting into two modes above 15 GPa and this may be related to the observed local structural modification in this study. It would be enlightening to carry out complementary FTIR measurements on such a hydrous olivine sample. The above initial findings may aid in refining the models for structural stability and compressibility (seismic velocities) of hydrous phases in the upper mantle.
ACKNOWLEDGMENTS

We thank Professor Quentin Williams for helpful comments for improving the manuscript. Thanks are due to John Balogh for maintaining the Raman system in good working order. This work was supported by US National Science Foundation grants EAR 0538884 and 0957137 to MHM, and EAR 11-13369 to JRS. Syntheses were performed at Bayerisches Geoinstitut, Universitaet Bayreuth, Germany, and supported, in part, by the Alexander von Humboldt Foundation to JS and FN. Portions of this work were performed at GeoSoilEnviroCARS (Sector 13), Advanced Photon Source (APS), Argonne National Laboratory. GeoSoilEnviroCARS is supported by the National Science Foundation - Earth Sciences (EAR-1128799) and Department of Energy - Geosciences (DE-FG02-94ER14466). Use of the Advanced Photon Source was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357. The SOEST and HIGP contribution numbers for this paper are xxxx and xxxx.
REFERENCES CITED


Angel, R.J. (2002) EOSFIT V5.2 program. Crystallography Laboratory, Virginia Tech, Blacksburg, USA.


-. (1991) Single crystal Raman spectra of forsterite, fayalite, and monticellite. American Mineralogist, 76(7-8), 1101-1109.


Kudoh, Y., Kuribayashi, T., Litasov, K., and Ohtani, E. (2007) Cation vacancies and possible hydrogen atom positions in Fe-bearing hydrous forsterite, Mg$_{1.85}$Fe$_{0.14}$Si$_{0.99}$H$_{0.06}$O$_4$, synthesized at 13.5 GPa and 1400 °C. Journal of Mineralogical and Petrological Sciences, 102(5), 306-310.


Table and Figure Captions

Table 1. Elastic properties of olivines.

Table 2. Unit-cell parameters of hydrous olivine Fo$_{97}$Fa$_3$ containing 4883 ppmw water (SZ0407A) and hydrous olivine Fo$_{97}$Fa$_3$ containing 8000 ppmw water (SZ0407B) as a function of pressure as determined by single-crystal X-ray diffraction.

Table 3. Mode frequencies (in cm$^{-1}$), mode Grüneisen parameters, and mode assignments for observed Raman modes of hydrous olivine Fo$_{97}$Fa$_3$ containing 4883 ppmw water (SZ0407A), and of anhydrous forsterite.

Figure 1. Unit-cell volumes of hydrous olivine Fo$_{97}$Fa$_3$ containing 4883 ppmw water (SZ0407A, open squares) and hydrous olivine Fo$_{97}$Fa$_3$ containing 8000 ppmw water (SZ0407B, open circles) as a function of pressure obtained from single-crystal XRD studies. Error bars are also shown in the Figure. Solid and dashed lines represent the two best-fit equations of state.

Figure 2. Unit-cell volumes of hydrous olivine Fo$_{97}$Fa$_3$ containing 4883 ppmw water (SZ0407A) as a function of pressure. Open symbols represent powder XRD data. Solid symbols are single-crystal XRD data. Solid and dashed lines represent the two best-fit equations of state, based on powder and single-crystal XRD, and single-crystal XRD, respectively. Note that the symbols are larger than the uncertainties.

Figure 3. Axial compressions $a/a_o$, $b/b_o$ and $c/c_o$ as a function of pressure for a hydrous olivine Fo$_{97}$Fa$_3$ containing 4883 ppmw water (SZ0407A) and for hydrous olivine Fo$_{97}$Fa$_3$ containing 8000 ppmw water (SZ0407B). Note that the symbols are larger than the uncertainties.

Figure 4. Raman spectra of hydrous olivine Fo$_{97}$Fa$_3$ containing 4883 ppmw water (SZ0407A) to 33.9 GPa.

Figure 5. Pressure dependences of the observed low frequency Raman modes for hydrous olivine Fo$_{97}$Fa$_3$ containing 4883 ppmw water (SZ0407A) from 200 ~ 750 cm$^{-1}$.

Figure 6. Pressure dependences of the four high frequency Raman modes for hydrous olivine Fo$_{97}$Fa$_3$ containing 4883 ppmw water (SZ0407A) from 800 ~ 1200 cm$^{-1}$.
Figure 7. Pressure dependence of Raman spectra of hydrous olivine Fo$_{97}$Fa$_3$ containing 4883 ppmw water (SZ0407A) in the OH-stretching region. The spectra are offset for clarity. The solid red line in the 1 bar spectrum is a fit using four Gaussian functions. Labels at right side indicate pressure in gigapascals and numbers on the 1 bar spectrum indicate O-H stretching mode frequencies obtained from the fit.

Figure 8. Pressure dependence of the Raman modes of hydroxyl group in hydrous olivine Fo$_{97}$Fa$_3$ containing 4883 ppmw water (SZ0407A).
### Table 1. Elastic properties of olivines

<table>
<thead>
<tr>
<th>Olivine composition</th>
<th>Method</th>
<th>Pressure range (GPa)</th>
<th>$K_s$ (GPa)</th>
<th>$K_s'$</th>
<th>$K_T$ (GPa)</th>
<th>$K_T'$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Anhydrous</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Forsterite (Fo₁₀₀)</td>
<td>Brillouin spectroscopy</td>
<td>32</td>
<td>129</td>
<td>4.2</td>
<td></td>
<td></td>
<td>Zha et al. (1998)</td>
</tr>
<tr>
<td>Forsterite (Fo₁₀₀)</td>
<td></td>
<td>Ambient pressure</td>
<td>129.5</td>
<td>4.65</td>
<td></td>
<td></td>
<td>Bass (1995)</td>
</tr>
<tr>
<td>Fo₀₉Fa₁</td>
<td>Ultrasonic</td>
<td>3 GPa</td>
<td>129.5</td>
<td>4.65</td>
<td></td>
<td></td>
<td>Bass (1995)</td>
</tr>
<tr>
<td>Fo₀₃Fa₇</td>
<td></td>
<td>Ambient pressure</td>
<td>129.4</td>
<td>4.65</td>
<td></td>
<td></td>
<td>Bass (1995)</td>
</tr>
<tr>
<td>Fo₀₃Fa₇</td>
<td></td>
<td>Ambient pressure</td>
<td>128.1</td>
<td>4.2</td>
<td></td>
<td></td>
<td>Bass (1995)</td>
</tr>
<tr>
<td>Fo₀₂Fa₈</td>
<td></td>
<td>126.7</td>
<td>126.7</td>
<td>4.2</td>
<td></td>
<td></td>
<td>Bass (1995)</td>
</tr>
<tr>
<td>San Carlos olivine Fo₉₀</td>
<td>Impulsive-stimulated scattering</td>
<td>12</td>
<td>129.4(5)</td>
<td>4.29</td>
<td>126.3</td>
<td>4.28</td>
<td>Abramson et al. (1997)</td>
</tr>
<tr>
<td>Forsterite (Fo₁₀₀)</td>
<td>Single-crystal XRD</td>
<td>17.2</td>
<td>125(2)</td>
<td>4.0(4)</td>
<td></td>
<td></td>
<td>Downs et al. (1996)</td>
</tr>
<tr>
<td>Forsterite (Fo₁₀₀)</td>
<td>Single-crystal XRD</td>
<td>15</td>
<td>122.6</td>
<td>4.3</td>
<td></td>
<td></td>
<td>Kudoh and Takéuchi (1985)</td>
</tr>
<tr>
<td>Forsterite (Fo₁₀₀)</td>
<td>Powder Synchrotron XRD</td>
<td>30</td>
<td>135.7(10)</td>
<td>3.9(10)</td>
<td></td>
<td></td>
<td>Will et al. (1986)</td>
</tr>
<tr>
<td><strong>Hydrous</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fo₀₉ (8000 ppmw H₂O)</td>
<td>Single-crystal XRD</td>
<td>8</td>
<td>120(2)</td>
<td></td>
<td></td>
<td></td>
<td>Smyth et al. (2005)</td>
</tr>
<tr>
<td>Fo₀₁₀₀ (0.8-0.9 wt% H₂O)</td>
<td>Brillouin scattering</td>
<td>125.7(2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Jacobsen et al. (2008, 2009)</td>
</tr>
<tr>
<td>Fo₀₇ (0.8-0.9 wt% H₂O)</td>
<td>Brillouin scattering</td>
<td>125.2(8)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Jacobsen et al. (2008, 2009)</td>
</tr>
<tr>
<td>Fo₀₇Fa₃ (4883 ppmw H₂O)</td>
<td>Single-crystal XRD</td>
<td>7</td>
<td>121.5(6)</td>
<td>5.6(2)</td>
<td></td>
<td></td>
<td>This study</td>
</tr>
<tr>
<td>Fo₀₇Fa₃ (8000 ppmw H₂O)</td>
<td>Single-crystal XRD</td>
<td>7</td>
<td>122.2(12)</td>
<td>6.4(10)</td>
<td></td>
<td></td>
<td>This study</td>
</tr>
<tr>
<td>Pressure (GPa)</td>
<td>SZ0407A</td>
<td>SZ0407B</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---------------</td>
<td>----------</td>
<td>----------</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$a$ (Å)</td>
<td>$b$ (Å)</td>
<td>$c$ (Å)</td>
<td>$V$ (Å³)</td>
<td>$V/V_0$</td>
<td>$a$ (Å)</td>
<td>$b$ (Å)</td>
</tr>
<tr>
<td>0.0001</td>
<td>4.759(3)</td>
<td>10.2238(2)</td>
<td>5.9932(1)</td>
<td>291.60(2)</td>
<td>1.00000</td>
<td>4.7624(6)</td>
<td>10.2260(3)</td>
</tr>
<tr>
<td>0.147(4)</td>
<td>4.7583(4)</td>
<td>10.2187(3)</td>
<td>5.9909(2)</td>
<td>291.30(3)</td>
<td>0.9990(1)</td>
<td>4.7624(6)</td>
<td>10.2209(3)</td>
</tr>
<tr>
<td>0.748(4)</td>
<td>4.7532(5)</td>
<td>10.1974(3)</td>
<td>5.9813(2)</td>
<td>289.91(3)</td>
<td>0.9942(1)</td>
<td>4.7572(6)</td>
<td>10.2003(3)</td>
</tr>
<tr>
<td>1.089(4)</td>
<td>4.7493(5)</td>
<td>10.1861(3)</td>
<td>5.9760(2)</td>
<td>289.10(3)</td>
<td>0.9914(1)</td>
<td>4.7544(7)</td>
<td>10.1883(3)</td>
</tr>
<tr>
<td>1.619(5)</td>
<td>4.7455(5)</td>
<td>10.1674(3)</td>
<td>5.9675(2)</td>
<td>287.93(3)</td>
<td>0.9874(1)</td>
<td>4.7503(6)</td>
<td>10.1698(3)</td>
</tr>
<tr>
<td>2.020(6)</td>
<td>4.7418(2)</td>
<td>10.1543(2)</td>
<td>5.9615(1)</td>
<td>287.04(1)</td>
<td>0.98436(5)</td>
<td>4.7461(6)</td>
<td>10.1561(3)</td>
</tr>
<tr>
<td>3.314(8)</td>
<td>4.7314(3)</td>
<td>10.1130(2)</td>
<td>5.9424(2)</td>
<td>284.33(2)</td>
<td>0.97508(6)</td>
<td>4.7365(6)</td>
<td>10.1152(3)</td>
</tr>
<tr>
<td>3.593(7)</td>
<td>4.7292(3)</td>
<td>10.1040(2)</td>
<td>5.9383(1)</td>
<td>283.75(2)</td>
<td>0.97309(6)</td>
<td>4.7341(6)</td>
<td>10.1066(2)</td>
</tr>
<tr>
<td>3.929(7)</td>
<td>4.7267(3)</td>
<td>10.0941(2)</td>
<td>5.9337(1)</td>
<td>283.11(2)</td>
<td>0.97088(6)</td>
<td>4.7322(7)</td>
<td>10.0963(3)</td>
</tr>
<tr>
<td>4.445(5)</td>
<td>4.7231(4)</td>
<td>10.0790(3)</td>
<td>5.9266(2)</td>
<td>282.13(2)</td>
<td>0.96750(8)</td>
<td>4.7288(6)</td>
<td>10.0813(2)</td>
</tr>
<tr>
<td>5.35(2)</td>
<td>4.7164(4)</td>
<td>10.0524(3)</td>
<td>5.9142(2)</td>
<td>280.40(3)</td>
<td>0.96157(9)</td>
<td>4.7222(6)</td>
<td>10.0553(2)</td>
</tr>
<tr>
<td>5.684(9)</td>
<td>4.7138(4)</td>
<td>10.0421(3)</td>
<td>5.9094(2)</td>
<td>279.73(3)</td>
<td>0.95929(9)</td>
<td>4.7190(8)</td>
<td>10.0448(3)</td>
</tr>
<tr>
<td>7.104(8)</td>
<td>4.7041(1)</td>
<td>10.0050(3)</td>
<td>5.8916(1)</td>
<td>277.27(2)</td>
<td>0.95084(6)</td>
<td>4.7109(5)</td>
<td>10.0073(2)</td>
</tr>
</tbody>
</table>
Table 3. Mode frequencies (in cm\(^{-1}\)), mode Grüneisen parameters, and mode assignments for observed Raman modes of hydrous olivine Fo\(_{97}\)Fa\(_{3}\) containing 4883 ppmw water (SZ0407A), with hydrous and anhydrous forsterite.

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Mode frequency</th>
<th>Mode Grüneisen Parameters</th>
<th>Mode frequency</th>
<th>Mode Grüneisen Parameters</th>
<th>Mode frequency</th>
<th>Mode Grüneisen Parameters</th>
<th>Mode type</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A_g)</td>
<td>227.0</td>
<td>0.88</td>
<td>228.4</td>
<td>0.689</td>
<td>226</td>
<td>0.674</td>
<td>SiO(_4) translation</td>
</tr>
<tr>
<td>(A_g)</td>
<td>302.5</td>
<td>1.62</td>
<td>305.6</td>
<td>1.31</td>
<td>304</td>
<td>1.63</td>
<td>M2 translation</td>
</tr>
<tr>
<td>(B_{2g})</td>
<td>325.2</td>
<td>1.65</td>
<td></td>
<td></td>
<td>323</td>
<td></td>
<td>Mix (M2 translation)</td>
</tr>
<tr>
<td>(B_{3g})</td>
<td>368.9</td>
<td>1.37</td>
<td></td>
<td></td>
<td>365</td>
<td></td>
<td>Mix (SiO(_4) rotation)</td>
</tr>
<tr>
<td>(B_{3g})</td>
<td>432.9</td>
<td>1.82</td>
<td>435.7</td>
<td>1.51</td>
<td>435</td>
<td>1.4</td>
<td>Mix (SiO(_4) rotation)</td>
</tr>
<tr>
<td>(A_g)</td>
<td>542.3</td>
<td>0.69</td>
<td>545</td>
<td>0.467</td>
<td>545</td>
<td>0.528</td>
<td>(\nu_4)</td>
</tr>
<tr>
<td>(B_{2g})</td>
<td>588.4</td>
<td>0.85</td>
<td>588.7</td>
<td>0.481</td>
<td>592</td>
<td></td>
<td>(\nu_4)</td>
</tr>
<tr>
<td>(A_g)</td>
<td>606.9</td>
<td>1.01</td>
<td>608.2</td>
<td>0.732</td>
<td>608</td>
<td>0.704</td>
<td>(\nu_4)</td>
</tr>
<tr>
<td>(A_g)</td>
<td>823.1</td>
<td>0.77</td>
<td>824.4</td>
<td>0.582</td>
<td>824</td>
<td>0.483</td>
<td>(\nu_1+\nu_3)</td>
</tr>
<tr>
<td>(A_g)</td>
<td>854.5</td>
<td>0.655</td>
<td>856.2</td>
<td>0.426</td>
<td>856</td>
<td>0.489</td>
<td>(\nu_1+\nu_3)</td>
</tr>
<tr>
<td>(B_{3g})</td>
<td>920.0</td>
<td>0.58</td>
<td>921</td>
<td></td>
<td>920</td>
<td>0.382</td>
<td>(\nu_3)</td>
</tr>
<tr>
<td>(A_g)</td>
<td>960.0</td>
<td>0.878</td>
<td>967</td>
<td>0.586</td>
<td>965</td>
<td>0.661</td>
<td>(\nu_3)</td>
</tr>
</tbody>
</table>
Figure 1. Unit-cell volumes of hydrous olivine Fo$_{0.7}$Fa$_3$ containing 4883 ppmw water (SZ0407A, open squares) and hydrous olivine Fo$_{0.7}$Fa$_3$ containing 8000 ppmw water (SZ0407B, open circles) as a function of pressure obtained from single-crystal XRD studies. Error bars are also shown in figure. Solid and dashed lines represent the two best-fit equations of state.

<table>
<thead>
<tr>
<th>Pressure (GPa)</th>
<th>Volume (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>294</td>
</tr>
<tr>
<td>1</td>
<td>291</td>
</tr>
<tr>
<td>2</td>
<td>288</td>
</tr>
<tr>
<td>3</td>
<td>285</td>
</tr>
<tr>
<td>4</td>
<td>282</td>
</tr>
<tr>
<td>5</td>
<td>279</td>
</tr>
<tr>
<td>6</td>
<td>276</td>
</tr>
<tr>
<td>7</td>
<td>273</td>
</tr>
<tr>
<td>8</td>
<td>270</td>
</tr>
</tbody>
</table>

K$_o$ = 121.5(6)
K$_o^{'}$ = 5.7(2)

K$_o$ = 122.3(12)
K$_o^{'}$ = 6.2(4)
Figure 2. Unit-cell volumes of hydrous olivine Fo$_{97}$Fa$_3$ containing 4883 ppmw water (SZ0407A) as a function of pressure. Open symbols represent powder XRD data. Solid symbols are single-crystal XRD data. Solid and dashed lines represent the two best-fit equations of state, based on powder and single-crystal XRD, and single-crystal XRD respectively. Note that the symbols are larger than the uncertainties.
Figure 3. Axial compressions $a/a_o$, $b/b_o$ and $c/c_o$ as a function of pressure for a hydrous olivine Fo$_{97}$Fa$_3$ containing 4883 ppmw water (SZ0407A) and for hydrous olivine Fo$_{97}$Fa$_3$ containing 8000 ppmw water (SZ0407B). Note that the symbols are larger than the uncertainties.
Figure 4. Raman spectra of hydrous olivine Fo$_{97}$Fa$_3$ containing 4883 ppmw water (SZ0407A) to 33.9 GPa.
Figure 5. Pressure dependences of the observed low frequency Raman modes for hydrous olivine Fo97Fa3 containing 4883 ppmw water (SZ0407A) from 200 ~ 750 cm$^{-1}$. 

- Ambient values:
  - 606.9 cm$^{-1}$
  - 588.4
  - 542.3
  - 432.9
  - 368.9
  - 325.2
  - 302.5
  - 227

- Mode Frequencies (cm$^{-1}$):
  - 608.4 + 3.1P
  - 586.3 + 2.9P - 0.011P$^2$
  - 545.4 + 1.3P + 0.051P$^2$
  - 430.7 + 5P - 0.022P$^2$
  - 374.8 + 3.7P - 0.033P$^2$
  - 328.6 + 3.1P
  - 306.6 + 4.0P - 0.055P$^2$
  - 227.3 + 1.2P - 0.006P$^2$
Figure 6. Pressure dependences of the four high frequency Raman modes for hydrous olivine Fo$_9$Fa$_3$ containing 4883 ppmw water (SZ0407A) from 800 ~ 1200 cm$^{-1}$. 
Figure 7. Pressure dependence of Raman spectra of hydrous olivine Fo97Fa3 containing 4883 ppmw water (SZ0407A) in the OH-stretching region. The spectra are offset for clarity. The solid red line in the 1 bar spectrum is a fit using four Gaussian. Labels at right side indicate pressure in gigapascals and numbers on the 1 bar spectrum indicate O-H stretching mode frequencies obtained from the fit.
Figure 8. Pressure dependence of the Raman modes of hydroxyl group in hydrous olivine Fo$_{97}$Fa$_{3}$ containing 4883 ppmw water (SZ0407A).