Effects of hydration on the elastic properties of olivine

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[1] Water, dissolved as hydroxyl (OH)− into the solid silicate minerals of the upper mantle can reduce adiabatic wave speeds through associated defects. Here we report Brillouin laser interferometry measurements of the speed of sound in single-crystal olivine containing 0.8–0.9 wt% H2O. The samples, synthesized at 12 GPa and 1200°C, represent nearly the maximum storage capacity of water in olivine at conditions of 350–400 km depth. The adiabatic (K30) and shear (G0) moduli of hydrous Fo100 are 125.7±0.2 GPa and 79.8±0.1 GPa, respectively. For hy-Fo100, we obtain K30 = 124.4±0.4 GPa and G0 = 75.3±0.3 GPa. Compared with anhydrous forsterite, the combined effects of 3 mol% Fe and 0.8 wt% H2O reduce bulk and shear moduli by 3.5±0.3% and 7.5±0.4% respectively, with greater reductions expected for more iron-rich Fo90 mantle compositions. Although lattice preferred orientation (LPO) studies have not been carried out under relevant conditions of pressure or water content, analysis of idealized single-crystal anisotropy for various known LPO types predicts up to 3% higher S-wave splitting anisotropy in hydrous olivine crystals aligned according to A-type and E-type fabrics, but no change in S-wave splitting anisotropy for B-type and C-type fabrics.


1. Introduction

[2] Hydrogen-related defects are known to influence the physical properties of mantle materials. Of particular relevance to geophysical studies are the effects of hydration on rheology [e.g., Mei and Kohlstedt, 2000; Jung et al., 2006], elasticity [e.g., Jacobsen, 2006], anelasticity [e.g., Karato and Jung, 1998], melting [e.g., Hirth and Kohlstedt, 1996], and electrical conductivity [e.g., Simpson and Tommasi, 2005]. Because the water-storage capacity of olivine approaches 1 wt% H2O at depths of 350–400 km [e.g., Smyth et al., 2006], the effects of hydration on the elastic properties of olivine are needed to evaluate seismic anomalous behavior of mantle materials under relevant conditions of water or pressure, analysis of idealized single-crystal anisotropy for various known LPO types predicts up to 3% higher S-wave splitting anisotropy in hydrous olivine crystals aligned according to A-type and E-type fabrics, but no change in S-wave splitting anisotropy for B-type and C-type fabrics. Water is known to significantly reduce the elastic and mechanical properties of olivine, but the incorporation of Al [e.g., Lemaire et al., 2004] and the formation of H0 [Hauri et al., 2006b] have been reviewed along with new observations from electron microscopy by Mosenfelder et al. [2006b]. X-ray structure refinements of hydrous olivine show mainly evidence for Mg2+ site vacancies [e.g., Smyth et al., 2006], whereas FTIR studies of hydrous olivine grown under varying silica activity suggest hydration mechanisms involving both Mg2+ and Si4+ vacancies [e.g., Lemaire et al., 2004; Mosenfelder et al., 2006b; Litaso et al., 2007].

[3] The defect structure and hydration mechanisms of olivine have been studied mainly by single-crystal X-ray diffraction, and inferred from polarized FTIR spectroscopy, and these have been reviewed along with new observations from high-pressure ultrasonic interferometry. Water is known to significantly reduce the elastic and mechanical properties of olivine, but the incorporation of Al [e.g., Lemaire et al., 2004] and the formation of H0 [Hauri et al., 2006b] have been reviewed along with new observations from electron microscopy by Mosenfelder et al. [2006b]. X-ray structure refinements of hydrous olivine show mainly evidence for Mg2+ site vacancies [e.g., Smyth et al., 2006], whereas FTIR studies of hydrous olivine grown under varying silica activity suggest hydration mechanisms involving both Mg2+ and Si4+ vacancies [e.g., Lemaire et al., 2004; Mosenfelder et al., 2006b; Litaso et al., 2007].

[4] The defect structure and hydration mechanisms of olivine have been studied mainly by single-crystal X-ray diffraction, and inferred from polarized FTIR spectroscopy, and these have been reviewed along with new observations from electron microscopy by Mosenfelder et al. [2006b]. X-ray structure refinements of hydrous olivine show mainly evidence for Mg2+ site vacancies [e.g., Smyth et al., 2006], whereas FTIR studies of hydrous olivine grown under varying silica activity suggest hydration mechanisms involving both Mg2+ and Si4+ vacancies [e.g., Lemaire et al., 2004; Mosenfelder et al., 2006b; Litaso et al., 2007].

[5] This paper deals mainly with the effects of hydration on elastic properties, without analysis of the olivine defect structure. Water is known to significantly reduce the elastic moduli of high-pressure olivine polymorphs, wadsleyite (β-Mg2SiO4), and ringwoodite (γ-Mg2SiO4). The elastic moduli of Mg-end member hydrous wadsleyite containing 1 wt% H2O show a 7.6% reduction in the bulk (K30) and 7.0% reduction in shear (G0) moduli [Mao et al., 2008]. The elastic moduli of Mg-end member hydrous ringwoodite containing 2.3 wt% H2O was studied to 23.4 GPa by Brillouin spectroscopy and show a reduction of 9% in the bulk and shear moduli compared with anhydrous Mg-ringwoodite [Wang et al., 2006]. The elastic properties of hydrous Fo80 ringwoodite containing 1 wt% H2O were measured by GHz-ultrasonic interferometry to 10 GPa, showing a 4.3% reduction in K30 and 14% reduction in G0 compared with anhydrous Mg-ringwoodite [Jacobsen and Smyth, 2006]. Because the addition of iron to anhydrous Mg2SiO4 polymorphs has a small, or slightly positive (increasing) effect on K30, but strongly reduces G [e.g., Sinogeikin et al., 1998], the net effect of adding iron and water to Mg-silicates is predominantly on shear properties, and consequently Vp/Vs ratios.

[6] The high water storage capacity of olivine at mantle conditions near the transition zone warrants investigation of
Table 1. Elastic Properties of Olivine with Varying Iron and Water Contenta

<table>
<thead>
<tr>
<th></th>
<th>Forsteriteb</th>
<th>San Carlos Olivinec</th>
<th>Effect of Fe (%)d</th>
<th>Hy-For100e</th>
<th>Effect of H2O (%)d</th>
<th>Hy-For97e</th>
<th>Effect of Fe and H2O (%)d</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg#</td>
<td>1.00</td>
<td>0.90</td>
<td>1.00</td>
<td>0.97</td>
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<tr>
<td>H2O (wt%f)</td>
<td>0</td>
<td>0</td>
<td>0.89</td>
<td>0.80</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cij (GPa)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C11</td>
<td>328.6(5)</td>
<td>320.2(4)</td>
<td>–2.6</td>
<td>315.4(6)</td>
<td>–4.0</td>
<td>306.7(14)</td>
<td>–6.7</td>
</tr>
<tr>
<td>C22</td>
<td>200.1(3)</td>
<td>195.9(3)</td>
<td>–2.1</td>
<td>195.3(5)</td>
<td>–2.4</td>
<td>191.9(11)</td>
<td>–4.1</td>
</tr>
<tr>
<td>C33</td>
<td>235.7(5)</td>
<td>233.8(3)</td>
<td>–0.8</td>
<td>234.4(7)</td>
<td>–0.6</td>
<td>227.2(20)</td>
<td>–3.6</td>
</tr>
<tr>
<td>C12</td>
<td>66.8(3)</td>
<td>67.9(3)</td>
<td>+1.6</td>
<td>64.8(6)</td>
<td>–3.0</td>
<td>63.8(15)</td>
<td>–4.5</td>
</tr>
<tr>
<td>C13</td>
<td>68.4(4)</td>
<td>70.5(3)</td>
<td>+3.1</td>
<td>67.2(6)</td>
<td>–1.8</td>
<td>67.9(13)</td>
<td>–0.7</td>
</tr>
<tr>
<td>C23</td>
<td>72.7(3)</td>
<td>78.5(4)</td>
<td>+8.0</td>
<td>70.2(6)</td>
<td>–3.4</td>
<td>73.3(14)</td>
<td>+0.8</td>
</tr>
<tr>
<td>C44</td>
<td>67.0(1)</td>
<td>63.5(2)</td>
<td>–5.2</td>
<td>66.0(3)</td>
<td>–1.5</td>
<td>62.0(8)</td>
<td>–7.5</td>
</tr>
<tr>
<td>C55</td>
<td>81.2(2)</td>
<td>76.9(2)</td>
<td>–5.3</td>
<td>80.2(2)</td>
<td>–1.2</td>
<td>76.3(6)</td>
<td>–6.0</td>
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<tr>
<td>C66</td>
<td>80.9(1)</td>
<td>78.1(1)</td>
<td>–3.5</td>
<td>78.7(4)</td>
<td>–2.7</td>
<td>71.6(9)</td>
<td>–11.5</td>
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<td>ρ (kg/m3)</td>
<td>3225</td>
<td>3350</td>
<td>+3.9</td>
<td>3180(3)</td>
<td>–1.4</td>
<td>3240(3)</td>
<td>+0.5</td>
</tr>
<tr>
<td>K50 (GPa)</td>
<td>128.9</td>
<td>129.5</td>
<td>+0.5</td>
<td>125.7(2)</td>
<td>–2.5</td>
<td>124.4(4)</td>
<td>–3.5</td>
</tr>
<tr>
<td>G9 (GPa)</td>
<td>81.4</td>
<td>77.5</td>
<td>–4.8</td>
<td>79.8(1)</td>
<td>–2.0</td>
<td>75.3(3)</td>
<td>–7.5</td>
</tr>
<tr>
<td>Vp (km/s)</td>
<td>5.85</td>
<td>8.34</td>
<td>–2.8</td>
<td>8.54(1)</td>
<td>–0.5</td>
<td>8.33(1)</td>
<td>–2.9</td>
</tr>
<tr>
<td>Vs (km/s)</td>
<td>5.02</td>
<td>4.81</td>
<td>–4.2</td>
<td>5.01(1)</td>
<td>–0.2</td>
<td>4.82(1)</td>
<td>–4.0</td>
</tr>
<tr>
<td>Vp/Vs</td>
<td>1.709</td>
<td>1.733</td>
<td>+1.4</td>
<td>1.705(5)</td>
<td>–0.3</td>
<td>1.728(6)</td>
<td>+1.1</td>
</tr>
<tr>
<td>Poisson, ν</td>
<td>0.239</td>
<td>0.251</td>
<td>+5.0</td>
<td>0.238(7)</td>
<td>–0.4</td>
<td>0.248(7)</td>
<td>+3.6</td>
</tr>
</tbody>
</table>

aValues in parentheses are standard deviations in the last place.
bSuzuki et al. [1983].
cWebb [1989].
dPercent change compared with anhydrous forsterite.
eThis study.
fWater contents estimated using the calibration of Bell et al. [2003].

the effects of hydration on its elastic properties. Here we report the elastic properties of forsterite (hy-For100) and hydrous olivine (hy-For97) containing what is considered to be the maximum possible concentration of water (0.9 wt% H2O) in olivine. The results, along with previous elasticity studies on forsterite (hy-For97) correspond to run SZ0407B of Smyth et al. [2006]. Both runs were carried out at 12 GPa and 1250°C (≈360 km depth), but the hy-For97 samples equilibrated with enstatite and melt, whereas the Fe-bearing hy-For97 composition equilibrated with clinochlore and melt. Thus, theSignificant in the fitting until a satisfactory and self-consistent fit was attained. For hy-For100, the fitted orientations match the plate directions from X-ray diffraction within 0.1 (hkl) in the plane with higher anisotropy (001), and to within about 0.3 (hkl) for the plane with lowest anisotropy (100), shown in Figure 1a. In total, we measured six platelets of hy-For97. The best self-consistency was achieved when the fit was conducted with nine non-zero elastic constants: C11, C22, C33, C12, C13, C23, C44, C55, and C66.

2. Experimental and Analytical Methods

[7] Hydrous olivine crystals were synthesized in the 5000-tonne multianvil press at Bayerisches Geoinstitut [Smyth et al., 2006]. The forsterite composition (hy-For100) corresponds to run SZ0408A, and the iron-bearing composition (hy-For97) corresponds to run SZ0407B of Smyth et al. [2006]. Both runs were carried out at 12 GPa and 1250°C (≈360 km depth), but the hy-For97 samples equilibrated with enstatite and melt, whereas the Fe-bearing hy-For97 composition equilibrated with clinochlore and melt. Thus, the hy-For100 and hy-For97 samples were annealed under conditions of relatively high, and low silica activity, respectively. Polarized FTIR measurements employing the calibration of Bell et al. [2003] were used to determine the water contents of the hy-For100 (0.89 wt% H2O) and hy-For97 (0.80 wt% H2O) samples (Table 1).

[8] For the Brillouin scattering measurements, 100–250 μm sized grains with optical clarity and clean extinction in cross-polarized light were oriented on a four-circle X-ray diffractometer. Plates parallel to (100), (010), and (001), and several randomly oriented grains were prepared for each composition. Crystals were double-polished (parallel faces) to 40–70 μm thickness, and 100–250 μm lateral dimensions. Brillouin spectra were obtained using a single-frequency, vertically polarized neodymium vanadate laser (λ = 532.15 nm) with a power of 150 mW at the sample using a six-pass Sandrock tandem Fabry-Perot interferometer in a forward symmetric scattering geometry. Acoustic velocities were determined by:

\[ V = \frac{\Delta \nu_B \lambda_0}{2 \sin(\theta/2)}, \]

where, λ0 is the incident laser wavelength, ΔνB is the measured Brillouin frequency shift and θ is the scattering angle external to the cell, which was 70(±0.03)° in this study. Each platelet was rotated about the axis bisecting the incident and collected light path and spectra were obtained every 5–10°, resulting in up to 28 velocity measurements (Vp and Vs) in each plane (Figure 1).

3. Results and Discussion

[9] The Christoffel equations [e.g., Every, 1980] were fitted to the measured phonon velocities and Eulerian angles defining the crystal orientation. Olivine is orthorhombic with nine non-zero elastic constants: C11, C22, C33, C12, C13, C23, C44, C55 and C66. For the hy-For100 composition, three platelets were measured with three Eulerian angles each, plus the nine elastic constants, totaling 18 parameters to fit. We used X-ray densities of 3180(±3) kg/m3 for the hy-For100 and 3240(±3) kg/m3 for the hy-For97 [Smyth et al., 2006]. We note that hydration of forsterite to 0.89 wt% H2O reduces its density by about 1.4% compared with anhydrous forsterite (Table 1). Both Cij and Eulerian-angle parameters were varied in the fitting until a satisfactory and self-consistent fit was attained. For hy-For100, the fitted orientations match the plate directions from X-ray diffraction within 0.1 (hkl) in the plane with higher anisotropy (001), and to within about 0.3 (hkl) for the plane with lowest anisotropy (100), shown in Figure 1a. In total, we measured six platelets of hy-For97. The best self-consistency was achieved when the fit was conducted with nine non-zero elastic constants: C11, C22, C33, C12, C13, C23, C44, C55, and C66.
obtained using the $b$-plate, $c$-plate, and a random plate of fitted orientation ($-0.9, -0.2, 0.4$), shown in Figure 1b.

The elastic constants of hy-Fo$_{100}$ and hy-Fo$_{97}$ are presented in Table 1, along with data for anhydrous forsterite [Suzuki et al., 1983] and San Carlos olivine [Webb, 1989] for comparison. Aggregate bulk and shear moduli were calculated from the fitted elastic constants using the Voigt-Reuss-Hill average. Referring to Table 1, the addition of 10 mol% iron to pure-Mg forsterite reduces elastic constants with $C_{ij}$ ($i = j$) by about 1–5%, whereas all
off-diagonal terms of the tensor $C_{ij}$ ($i \neq j$) increase by about 2–8%. The addition of 0.8 wt% H$_2$O to forsterite in our hy-Fo$_{100}$ samples shows a reduction of all $C_{ij}$ by 0.6–4.0%. For hy-Fo$_{100}$, we obtain $K_{SO} = 125.7(\pm0.2)$ GPa and $G_0 = 79.8(\pm0.1)$ GPa, which are about 2.5% and 2.0% lower than anhydrous forsterite, respectively.

[11] Comparing the $C_{ij}$ of hy-Fo$_{07}$ with anhydrous Fo$_{100}$ to ascertain the net effect of iron and hydration shows that there is a large reduction in most $C_{ij}$ by 4–12%, except for $C_{13}$ and $C_{23}$, which are unchanged within error. For hy-Fo$_{07}$, we obtain $K_{SO} = 124.4(\pm0.4)$ GPa and $G_0 = 75.3(\pm0.3)$ GPa, which are 3.5% and 7.5% lower than anhydrous forsterite. The overriding trend is that addition of iron to forsterite has minimal or slightly positive effect on $K_{SO}$, but strongly reduces $G_0$, whereas the addition of water reduces both. Compared with pure-forsterite, addition of $\sim$10 mol% Fe in San Carlos olivine reduces $V_p$ and $V_s$ by 2.8% and 4.2% respectively (Table 1). The hy-Fo$_{07}$ velocities (with only 3 mol% Fe) are 2.9% and 4.0% lower than anhydrous forsterite, suggesting that hydrous Fo$_{07}$ olivine, closer to mantle composition, would exhibit even further reduced velocities.

[12] The effects of water on elastic moduli and acoustic velocities of olivine are plotted in Figure 2, along with other minerals of the olivine-brucite join, $n$[Mg$_2$Si$_{1-x}$O$_{3-x}$ · Mg(OH)$_2$], where $n = 2$ for chondrodite, $n = 4$ for clinohumite, and Mg(OH)$_2$ is the mineral brucite. In Figure 2, pure-Mg compositions are plotted with open symbols, and filled symbols are used for Fe-bearing compositions. Because the effects of iron on bulk moduli are small, we fitted a linear variation of bulk modulus with water content using all the data, shown by the dashed line in Figure 2a:

$$K_0(\text{GPa}) = 127.3(\pm0.8) - 2.0(\pm0.2)C_{12}$$

where $C_{12}$ is the water content in weight percent. Because iron has a large influence on shear moduli, we fitted a linear variation of shear modulus with water content separately for Fe-bearing phases along the olivine-brucite join yielding,

$$G_0(\text{GPa}) = 76.6(\pm0.6) - 1.3(\pm0.1)C_{12}$$
In Figure 2b, we show linear trends for the compressional and shear wave velocities for iron-bearing phases along the olivine-brucite join, resulting in:

$$\text{Vp}(\text{km/s}) = 8.35(\pm 0.01) - 0.035(\pm 0.002)C_{\text{H2O}}$$  

(4)

$$\text{Vs}(\text{km/s}) = 4.81(\pm 0.02) - 0.025(\pm 0.003)C_{\text{H2O}}$$  

(5)

4. Anisotropy

Seismic-wave anisotropy is one of the most robust geophysical observations used to infer flow geometry in the mantle. If orthorhombic olivine crystals align in lattice preferred orientation (LPO) under a given flow field, several types of anisotropy can occur. Although LPO studies have not been carried out at conditions relevant to the deep upper mantle with such high water contents, here we analyze the current results for various known types of LPO. In a horizontal flow field, P-waves travelling vertically through the field will exhibit slower velocities than P-waves propagating parallel to flow, called Pn-type anisotropy, if the fast Vp[100] axis of olivine is preferentially aligned parallel to the flow, as in A-type LPO [e.g., Jung et al., 2006]. The effects of iron and hydration on Vp in various crystallographic directions of olivine are listed in Table 2. Hydration of forsterite slightly reduces the maximum P-wave anisotropy, expressed as [(Vmax − Vmin)/Vmean] × 100, from 25.1 (+0.4)% to 24.1 (+0.1)% in the hy-Fo97 sample. The same sample is shown to reduce P-wave anisotropy of 23.6 (+0.4)%.

In order to analyze the effects of hydration on shear-wave splitting anisotropy, we consider the idealized case of a single crystal aligned in a horizontal flow field with S-waves propagating in the plane of shear and polarized either in the shear plane (VSH) or perpendicular to the shear plane (VSV). In Table 2, Vs is given for each of the two possible purer-mode polarization directions for a given propagation direction parallel (//) to the a-axis, b-axis, and c-axes of olivine. The S-wave splitting anisotropy for anhydrous forsterite and San Carlos olivine with Vs // b- and c-axes is ∼10%, whereas S-waves propagating along the a-axis of olivine show little or no shear-wave splitting anisotropy, which is why this direction is chosen as the axis of symmetry in hexagonal transverse isotropy. Compared with anhydrous forsterite, the results for hy-Fo100 show hydration increases the S-wave splitting anisotropy from about 0.2% to 0.9% in the a-axis direction, but reduces S-wave splitting from about 9.4% to 8.8% for S-waves propagating in the b-axis direction, although we note that these differences are not drastic considering experimental uncertainty. The hy-Fo100 exhibits similar S-wave splitting anisotropy in the c-axis direction as anhydrous forsterite.

In addition to type-A fabric associated with low-water conditions, Jung et al. [2006] described three newly observed fabric types; type-B associated with high-stress and/or moderate to high water contents, type-C associated with low-stress and water-rich conditions, and type-E associated with low-stress and moderate water contents. In both cases (type-B and type-C) there is essentially no change in S-wave splitting anisotropy with hydration (Table 2) but because the c-axis is sub-parallel to flow, the Pn-type anisotropy would instead show fast vertical propagating P-waves compared with the direction of shear. In the case that type-A fabric persisted under hydrous conditions, Pr-type anisotropy would still display fast P-waves in the direction of shear, but S-wave splitting anisotropy would be greater than under anhydrous conditions. Future studies of LPO at deeper mantle pressures and under more hydrous conditions are needed to determine what type of LPO might be relevant near the transition zone. In addition, pressure and temperature derivatives of the elastic moduli of hydrous olivine are needed in order to provide a more robust prediction of possible seismological signatures of hydration in the deep upper mantle.

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