First-principles investigation of hydrous post-perovskite

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A R T I C L E   I N F O

Article history:
Received 8 September 2014
Received in revised form 20 January 2015
Accepted 26 March 2015
Available online 11 April 2015

Keywords:
Hydrogen
Post-perovskite
Lower mantle
Elasticity

A B S T R A C T

A stable, hydrogen-defect structure of post-perovskite (hy-ppv, MgSi2−xHxO) has been determined by first-principles calculations of the vibrational and elastic properties up to 150 GPa. Among three potential hy-ppv structures analyzed, one was found to be stable at pressures relevant to the lower-mantle D0 region. Hydrogen has a pronounced effect on the elastic properties of post-perovskite due to magnesium defects associated with hydration, including a reduction of the zero-pressure bulk (K0) and shear (G0) moduli by 5% and 8%, respectively, for a structure containing ~1 wt.% H2O. However, with increasing pressure the moduli of hy-ppv increase significantly relative to ppv, resulting in a structure that is only 1% slower in bulk compressional velocity and 2.5% slower in shear-wave velocity than ppv at 120 GPa. In contrast, the reduction of certain anisotropic elastic constants (Cij) in hy-ppv increases with pressure (notably, C55, C66, and C23), indicating that hydration generally increases elastic anisotropy in hy-ppv at D0 pressures. Calculated infrared absorption spectra show two O–H stretching bands at ~3500 cm−1 that shift with pressure to lower wavenumber by about 2 cm−1/GPa. At 120 GPa the hydrogen bonds in hy-ppv are still asymmetric. The stability of a hy-ppv structure containing 1–2 wt.% H2O at D0 pressures implies that post-perovskite may be a host for recycled or primordial hydrogen near the Earth’s core-mantle boundary.

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1. Introduction

Seismic investigations of the lowermost several hundred kilometers of the mantle (called the D0 region) have revealed a heterogeneous region with large-scale structures including large low-shear-velocity provinces (LSVPs) and ultralow-velocity zones (ULVZs) overlying the core (Garnero and McNamara, 2008). However, the influence of hydrogen on ppv structure and physical properties has not been determined.

The composition and mineralogy of D0 remains unresolved due to uncertainties in core-mantle boundary (CMB) temperature (Nomura et al., 2014), spatial heterogeneity of D0 material (e.g. slab graveyards) (Garnero and McNamara, 2008), and the effect of major element substitution on physical properties of the brg/ppv phase boundary for candidate lower mantle compositions (Grocholski et al., 2012).

Previous studies have investigated the effect of major-element substitution on the bridgmanite to post-perovskite phase transition and on physical properties of post-perovskite (Murakami and Hirose, 2005; Mao et al., 2006; Grocholski et al., 2012). In Al-free systems, increasing Fe2+ decreases the pressure of the phase boundary, whereas increasing Fe3+ and Al-content suppresses the phase boundary to higher pressures (greater depths) (Grocholski et al., 2012). The brg to ppv transition should occur above the CMB in harzburgite and MORB but potentially below the CMB conditions in pyrolite (Grocholski et al., 2012). However, the influence of hydrogen on ppv structure and physical properties has not been determined.

The bulk H2O content of the mantle is among the least well constrained compositional parameters of the Earth, with estimates varying by orders of magnitude due to uncertainty in the bulk mantle and core hydrogen content (e.g. Williams and Hemley, 2001). The water storage capacity of the uppermost mantle varies with depth, but in the peridotite system olivine and pyroxene can contain about 0.1 wt.% H2O at 400 km depth (Tenner et al., 2012; Ferot and Bolfan-Casanova, 2012). The transition zone water storage capacity is likely much higher because wadsleyite and ringwoodite can incorporate 1–2 wt.% H2O into their structures (Bolfan-Casanova et al., 2000; Inoue et al., 2010; Kohlstedt et al., 1996). The recent discovery of a hydrous ringwoodite inclusion in diamond containing ~1.5 wt.% H2O suggests the transition zone...
may be very hydrous, at least locally (Pearson et al., 2014). The H$_2$O storage capacity of the lower mantle remains highly uncertain due to conflicting estimates of H$_2$O storage capacity of bridgmanite, which range from about 0.001 wt.% (Bolfan-Casanova et al., 2003) to 0.4 wt.% (Murakami et al., 2002) and values in between (Litasov et al., 2003). A recent computational investigation by Hernandez et al., 2013 calculated the hydrogen partition coefficient between ringwoodite, ferropericlase, and bridgmanite and estimated that bridgmanite may contain up to 1000 ppm (0.1 wt.% water). Contrast in the H$_2$O storage capacity between ringwoodite and bridgmanite may lead to dehydration melting below the 660 km discontinuity and provide evidence for regional scale hydration of the transition zone (Schmament et al., 2014).

In contrast to bridgmanite, the post-perovskite structure is potentially more accommodating of hydrogen because both oxygen sites of the structure are slightly under-bonded. Magnesium is coordinated to eight oxygens with interatomic distances less than 2 Å and to two oxygens with distances slightly longer than 2 Å (Zhang et al., 2013). If the two longer oxygens are excluded from the Pauling bond strength sum, both O1 and O2 have the potential to protonate with charge balance achieved by an Mg-site vacancy. To test the idea that ppv may store seismically detectable amounts of hydrogen at D' pressures, we have investigated several potential hydrous post-perovskite structures using density functional theory (DFT). We describe the most favorable hy-ppv structure and calculate its elastic and vibrational properties under static conditions in order to determine its mechanical stability, single-crystal and bulk-elastic wave velocities, and infrared absorption spectra.

2. Methods

Post-perovskite is orthorhombic with space group Cmcm (Murakami et al., 2004; Tsuchiya et al., 2004; Oganov and Ono, 2004). The structure contains alternating layers of corner-sharing SiO$_6$ octahedra and Mg polyhedra in eight coordination to oxygen (Murakami et al., 2004; Zhang et al., 2013). DFT calculations were carried out using the PWSCF code, part of the Quantum ESPRESSO package using the Perdew–Ernzerhof–Burke generalized gradient approximation (Hohenberg, 1964; Kohn and Sham, 1965; Perdew et al., 1996; Giannozzi et al., 2009). Wavefunctions were expanded with plane waves using an energy cutoff of 100 Ry. Norm-conserving pseudopotentials were used to describe H, O, and Si (Troullier and Martins, 1991). The Mg pseudopotential was generated by the method of U. von Barth and R. Car and has been used in previous investigations of hydrogen in silicates (Karki and Wentzcovitch, 2000; Blanchard et al., 2005; Verma and Karki, 2009; Brodholt and Refson, 2000; Umemoito et al., 2011).

3. Results and discussion

Three potential OH-defect structures of post-perovskite were studied by positioning hydrogen in a magnesium vacancy of the ppv supercell using the electron localization function (Gibbs et al., 2003) to identify initial H positions. The first model (hy-ppv1) features one OH–H group and one O2–H group, the second (hy-ppv2) features two approximately symmetric O2–H groups, and the third model (hy-ppv3) features two asymmetric O2–H groups. After calculation of phonons and enthalpy under 0 K conditions via density functional perturbation theory under the linear-response theory of Baroni et al., 2001, in which the dynamical matrix along with dielectric quantities such as the Born effective charge tensor are evaluated at the Γ-point. The scheme outlined above is similar to previous ab initio calculations of IR spectra for hydrous silicates (Karki and Wentzcovitch, 2000; Blanchard et al., 2005; Verma and Karki, 2009; Brodholt and Refson, 2000; Umemoito et al., 2011).

![Fig. 1. Predicted stable hydrogen defect structure of hy-ppv at 120 GPa. Left: view of hy-ppv down the a-axis. Right: electron localization function 93-percentile iso-surface (green) of a Mg vacancy site in hy-ppv with super-imposed hydrogen groups. Atom positions are shown as oxygen (red), silicon (blue), magnesium (orange), and hydrogen (black). Lattice parameters and hydrogen-bond distances of the structure at 0 and 120 GPa are listed in Table 1. Fractional coordinates of atom positions for all structures are provided in the Supplementary materials. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)](image-url)
modes, and hy-ppv2, although stable, has a higher enthalpy than hy-ppv3 at 0 K at all pressures considered in this study (by about 0.10 eV per formula unit).

The stable structure of hy-ppv at 120 GPa is illustrated in Fig. 1. At 0 GPa, the O–H bond distance is 0.98 Å, with a hydrogen bond geometry of $d(O\cdot\cdot\cdotO) = 2.17$ Å, $d(O\cdot\cdot\cdotH) = 2.73$ Å, and hydrogen bond angle 115°. For comparison, the hydrogen-bond geometry in hydrous bridgmanite (Hernandez et al., 2013) is $d(O\cdot\cdot\cdotH) = 1.1$ Å, $d(O\cdot\cdot\cdotO) = 1.65$ Å, with a hydrogen-bond angle of about 150°. Thus, the hydrogen bond in hy-ppv is considerably more non-linear than in hy-brg. In hy-ppv, the O–H bond distance increases slightly with pressure as the hydrogen bond distance $d(O\cdot\cdot\cdotO)$ shortens, consistent with general trends among hydrogen bonds in minerals (Libowitzky, 1999). Lattice parameters, energies, and hydrogen-bond geometry of hy-ppv at 0 and 120 GPa are listed in Table 1. Fractional coordinates of all the atom positions in all structures and all pressures are provided in the Supplementary materials.

The effect of hydrogen on the elastic tensor of ppv is shown in Fig. 2. Generally $C_{44}$, $C_{55}$, $C_{66}$, and $C_{23}$ are relatively insensitive to hydration at D00 pressures, while $C_{11}$, $C_{22}$, $C_{33}$, $C_{12}$, and $C_{13}$ are more sensitive to hydration. At 120 GPa $C_{22}$ and $C_{33}$ are reduced by approximately 0.1% while $C_{66}$ is reduced by approximately 20% with addition of 2.31 wt.% H2O. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

### Table 1

<table>
<thead>
<tr>
<th>Structure</th>
<th>$P$ (GPa)</th>
<th>$a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
<th>$V$ ($Å^3$)</th>
<th>$E$ (eV/FU)</th>
<th>$d(O\cdot\cdot\cdotH)$ (Å)</th>
<th>$d(O\cdot\cdot\cdotO)$ (Å)</th>
<th>$d(H\cdot\cdot\cdotO)$ (Å)</th>
<th>H-bond angle (°)</th>
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<td>2.7020</td>
<td>9.1539</td>
<td>6.6966</td>
<td>165.6342</td>
<td>-1470.0485</td>
<td>0.9838</td>
<td>2.734</td>
<td>2.172</td>
<td>114.67</td>
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<td>9.1891</td>
<td>6.6867</td>
<td>166.3856</td>
<td>-1470.0176</td>
<td>0.9838</td>
<td>2.734</td>
<td>2.172</td>
<td>114.67</td>
</tr>
<tr>
<td>hy-ppv (2.31 wt.%)</td>
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<td>2.7173</td>
<td>9.2101</td>
<td>6.6744</td>
<td>167.0391</td>
<td>-1469.9448</td>
<td>0.9866</td>
<td>2.724</td>
<td>2.160</td>
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</table>

**Fig. 2.** Elastic tensor components (using Voigt notation) of ppv (black) and hy-ppv (1.14 wt.% H2O in blue, 2.31 wt.% H2O in red). $C_{22}$, $C_{33}$, $C_{12}$, and $C_{13}$ are relatively insensitive to hydration at D00 pressures, while $C_{11}$, $C_{44}$, $C_{55}$, $C_{66}$, and $C_{23}$ are more sensitive to hydration. At 120 GPa $C_{22}$ and $C_{33}$ are reduced by approximately 0.1% while $C_{66}$ is reduced by approximately 20% with addition of 2.31 wt.% H2O.
hydration, with the most sensitive component $C_{66}$ reduced by 20% at 120 GPa for the 2.31 wt.% $H_2O$ hy-ppv structure. We used the Born stability criteria to determine the mechanical stability of hy-ppv compared to ppv (Born and Huang, 1954). In the case of orthorhombic symmetry, these criteria reduce to the following:

$$B_{1,i} = C_{ii} > 0 \quad (i = 1, 2, 3, \ldots, 6)$$

$$B_{2,ij} = \det \begin{bmatrix} C_{ii} & C_{ij} \\ C_{ji} & C_{jj} \end{bmatrix} > 0 \quad (i, j = \{1, 2, 3\}, \ i \neq j)$$

$$B_3 = \det \begin{bmatrix} C_{11} & C_{12} & C_{13} \\ C_{21} & C_{22} & C_{23} \\ C_{31} & C_{32} & C_{33} \end{bmatrix} > 0$$

The Born stability criteria calculated for pure ppv and hy-ppv are shown in Fig. 3 and indicate that hydrogen does not destabilize the post-perovskite lattice over lower mantle pressures for a simple Mg:2H substitution.

Bulk elastic properties for ppv and hy-ppv were calculated from the single-crystal elastic tensors using the Voigt–Reuss–Hill averaging scheme and are shown in Fig. 4 (Hill, 1952). The Hill-averaged elastic wave velocities decrease with hydration, as expected, but the bulk sound velocity ($V_U$) is remarkably insensitive to the presence of hydrogen. At 120 GPa, $V_U$ is reduced by 8 m/s per wt.% $H_2O$ (<0.1% decrease). In contrast to the bulk sound velocity, both the Hill-averaged $P$-wave ($V_P$) and $S$-wave ($V_S$) velocities decrease by approximately 68 m/s per wt.% $H_2O$ (0.5% decrease) and 85 m/s per wt.% $H_2O$ (1.1% decrease), respectively, at 120 GPa. Of particular note is that at 120 GPa the $S$-wave velocity of hy-ppv is slower than that of ppv and brg (for the 2.31 wt.% $H_2O$ model), implying that a very hydrous hy-ppv, if present in D$^\prime$, may be difficult to distinguish from bridgmanite using bulk sound velocity and/or shear-wave profiles alone.

The Hill averages of the bulk and shear moduli of ppv decrease linearly with water content, as shown in Fig. 5. At 0 GPa, the bulk modulus of ppv decreases by 9.6 GPa per wt.% $H_2O$, corresponding to 4.5% reduction per wt.% $H_2O$ relative to the dry ppv $K_0 = 214$ GPa. The effect of water on the bulk modulus is significantly less at 120 GPa, with about 7.4 GPa reduction per wt.% $H_2O$, corresponding to only about 1% reduction in $K$ per wt.% $H_2O$ relative to the dry $K_{120} = 677$ GPa. In contrast, the shear modulus decreases by 9.3 GPa per wt.% $H_2O$ at 0 GPa, corresponding to a

Fig. 3. Born stability criteria for ppv (black), and hy-ppv (1.14 wt.% $H_2O$ in blue and 2.31 wt.% $H_2O$ in red). Mechanical stability of the lattice requires each quantity be greater than zero. Addition of hydrogen to the ppv lattice does not destabilize the ppv structure. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 4. Bulk elastic properties of brg (dashed), ppv (black), and hy-ppv (1.14 wt.% $H_2O$ in blue, 2.31 wt.% $H_2O$ in red). Voigt–Reuss–Hill averaged bulk modulus and shear modulus (top), and bulk wave velocities (bottom). Bulk sound velocity is relatively insensitive to hydrogen content, while bulk shear velocity is most sensitive. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 5. Top: dependence of bulk modulus (top) and shear modulus (bottom) upon water content for ppv at 0 and 120 GPa.
8.1% reduction per wt.% H₂O relative to the dry G₀ = 114 GPa. At 120 GPa, the shear modulus decreases by 10.3 GPa per wt.% H₂O, corresponding to about 3.1% reduction per wt.% H₂O relative to the dry G₁₂₀ = 336 GPa. For comparison, the bulk modulus K₀ = 203 GPa for Mg hy-ppv containing ~1 wt.% H₂O is 25% lower than the K₀ = 272 GPa reported for anhydrous (Mg₀.6Fe₀.4)-ppv (Mao et al., 2006). The reduction in K₀ (4.5%) and G₀ (8.1%) per wt.% H₂O for ppv upon hydration is about half that of ringwoodite, with about 15% reduction in G₀ per wt.% H₂O (Jacobsen et al., 2004). However, one of the most important results of the current calculations is that at pressures of D₀₀, the calculated reduction by 1 wt.% H₂O in ppv is only about 1% in K and only about 3% in G, indicating that the hy-ppv structure is very stiff even in comparison with dry ppv. The combined influence of hydration, Al, and Fe-content in ppv remains to be explored in future work.

At D₀₀ conditions, the effects of hydration on the Hill average of the bulk and shear moduli can be compared with the influence of temperature by applying the temperature derivatives of the moduli for ppv reported by Stackhouse et al., 2005. At 120 GPa, the influence of 1 wt.% H₂O on the bulk modulus is equivalent to raising the temperature by about 300 K, whereas the effect of 1 wt.% H₂O on the shear modulus is comparable to increasing temperature by about 675 K. There is very little effect of hydration on the VP/VS ratio of ppv, which shows about 0.01 increase (~0.5%) both at 0 and 120 GPa for 1 wt.% H₂O (Table 2).

The single crystal elastic wave velocities were calculated using the Cristoffel equation:

\[
\text{det}(c_{ijkl} n_i n_j - \rho V^2 \delta_{ij}) = 0
\]

where \(c_{ijkl}\) is the elastic tensor, \(n\) is the propagation direction, \(\rho\) is the density, \(V\) is the velocity, and \(\delta_{ij}\) is the Kronecker delta (Musgrave, 1970). The effect of H on the single crystal elastic wave velocities calculated from Eq. (4) at 0 and 120 GPa are shown in Fig. 6. The full elastic tensor and density at 0 and 120 GPa are listed in Table 2. At all pressures the presence of hydrogen reduces the elastic wave velocities for both P and S phases; however, the S-wave

<table>
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<th>P (GPa)</th>
<th>C₁₁ (GPa)</th>
<th>C₂₂ (GPa)</th>
<th>C₃₃ (GPa)</th>
<th>C₄₄ (GPa)</th>
<th>C₅₅ (GPa)</th>
<th>C₆₆ (GPa)</th>
<th>C₁₂ (GPa)</th>
<th>C₁₃ (GPa)</th>
<th>C₂₃ (GPa)</th>
<th>ρ (kg/m³)</th>
<th>Vₚ (km/s)</th>
<th>Vₛ (km/s)</th>
<th>K (GPa)</th>
<th>G (GPa)</th>
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<td>40</td>
<td>79</td>
<td>101</td>
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<td>5.33</td>
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<td>114</td>
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<td>1295</td>
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<td>266</td>
<td>416</td>
<td>433</td>
<td>342</td>
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<td>5435</td>
<td>14.38</td>
<td>7.86</td>
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<td>336</td>
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Table 2
Pressure dependence of elastic properties, density, and Hill-averaged bulk wave velocities of ppv and hy-ppv. Elastic tensor, density, and elastic wave velocities at all pressures can be found in Supplementary materials.

Table 3
Equation-of-state parameters of post-perovskite with varying hydrogen content. Bulk modulus (Kₑₙ) and its pressure derivative (K₀) were fit using a 3rd-order Birch-Murnaghan equation of state.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Kₑₙ (GPa)</th>
<th>K₀ (GPa)</th>
<th>V₁₀ (cm³/mol)</th>
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<td>ppv</td>
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<td>24.94</td>
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<tr>
<td>hy-ppv (1.14 wt.% H₂O)</td>
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<td>4.28</td>
<td>25.05</td>
</tr>
<tr>
<td>hy-ppv (2.31 wt.% H₂O)</td>
<td>191</td>
<td>4.32</td>
<td>25.15</td>
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</table>

Fig. 6. Single crystal elastic wave velocities calculated for dry ppv (black), 1.14 wt.% H₂O (blue), and 2.31 wt.% H₂O (red). The presence of hydrogen has a pronounced effect on S-wave velocities relative to P-wave velocities. The presence of hydrogen does not noticeably change the minimum or maximum velocity directions. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 7. Top: vibrational density of states for hy-ppv (1.14 wt.% H₂O) at 120 GPa. Bottom: calculated IR absorption spectra of hy-ppv at mantle pressures. Low-wavenumber peaks are lattice modes, and the two high-wavenumber peaks are characteristic of OH, representing in-phase stretching (low) and out-of-phase stretching (high).
velocities are more sensitive to hydration. At 120 GPa the single crystal \(V_F\) is generally unchanged by hydration while \(V_S\) is reduced by 1.2% per wt.% H\(_2\)O.

All ppv and hy-ppv structures were fit to 3rd-order Birch-Murnaghan equations of state (EOS), and EOS parameters are given in Table 3. At 0 GPa the addition of 1.14 wt.% H\(_2\)O increases the molar volume of ppv by 0.5%, and addition of 2.31 wt.% H\(_2\)O increases the molar volume by 0.9%. For comparison, the Mg end-member hydrous ringwoodite containing 2.2 wt.% H\(_2\)O studied by Inoue et al., 1998 had a molar volume 0.27% larger than dry Mg-ringwoodite (Weidner et al., 1984). Thus, at 0 GPa, the increase in molar volume due to hydration of ppv is about four times that of ringwoodite. However, due to the increased compressibility of the hy-ppv phase, at 120 GPa the 1.14 wt.% H\(_2\)O hy-ppv structure has a molar volume that is 0.3% smaller than dry ppv, and the 2.31 wt.% H\(_2\)O hy-ppv structure has a molar volume that is 0.7% smaller than dry ppv.

Calculated vibrational density of states and infrared absorption spectra of hy-ppv are shown in Fig. 7. Two O–H stretching bands of hy-ppv are observed at 3492 and 3506 cm\(^{-1}\) at ambient pressure and correlate well with OH vibrational frequencies found in other high-pressure silicates (Libowitzky, 1999). With pressure these bands shift linearly with \(d\nu_{3492}/dP = -2.25 \text{ cm}^{-1}/\text{GPa}\) and \(d\nu_{3506}/dP = -1.94 \text{ cm}^{-1}/\text{GPa}\). In contrast to phase D we do not see hydrogen bond symmetrization in hy-ppv even at lower mantle pressures (Tsuchiya et al., 2005). The negative pressure shift of the OH modes is commonly observed in previous studies and occurs because the hydrogen bonds become more symmetric with increasing pressure which lengthens the \(O–H\) bond, thereby reducing the frequency (Libowitzky, 1999). The lower-frequency mode corresponds to in-phase stretching of the two OH groups, and the higher-frequency mode corresponds to 180-degree-out-of-phase stretching between the two OH groups. Measurements of OH in minerals at lower mantle pressures using current techniques is challenging, but experimental observation of OH in ppv may be especially challenging because ppv is not stable at low pressure (Mao et al., 2006), where many experimental measurements of OH in minerals are carried out.

4. Summary

Recent estimates of the return flux of water to the mantle via subduction suggest that perhaps several hundreds of ppm water may be retained in the slab beyond the depth of magma generation (Parai and Mukhopadhyay, 2012; Garth and Rietbrock, 2014). If slabs carry water through the lower mantle and into D\(^\prime\), then ppv, the major silicate mineral in D\(^\prime\), may be a potential host for water.

Primordial components, such as noble gases, in some ridge basalts may imply that magmas deriving from the deep mantle sample unmixed source regions (Craig et al., 1978; Gonnermann and Mukhopadhyay, 2007). The descent of slabs to the core mantle boundary (e.g. Garnero and McNamara, 2008) provides a mechanism of water incorporation into the D\(^\prime\) region, through both nominally anhydrous minerals and potential stability of dense hydrous magnesium silicates such as phase H to lower mantle conditions (Nishi et al., 2014). Though the equilibrium assemblage of hydrous minerals under lower mantle conditions is not well known, and we therefore cannot comment on the most likely host for water in D\(^\prime\), this study has shown for the first time that a stable structure of hy-ppv persists to D\(^\prime\) pressures and displays modified elastic properties which may make it difficult to distinguish from brg using \(V_s\) profiles alone.

The stability of a hy-ppv structure containing 1–2 wt.% H\(_2\)O at D\(^\prime\) pressures implies that post-perovskite can potentially host a significant amount of recycled or primordial hydrogen near the Earth’s core-mantle boundary. Future research requires determination of the hydrogen partition coefficient between post-perovskite and other lower mantle phases such as bridgmanite, especially with more realistic compositions that include iron and aluminum. Further constraints on the effects of hydration on the mechanical and elastic properties of post-perovskite, especially at high temperature, will be important for future work that may provide insight into the fate of water in the seismically heterogeneous core-mantle boundary region.

Acknowledgements

JPT was supported by the EAPSI Program of the U.S. National Science Foundation (NSF) Grant Number 1209633 and the Japan Society for the Promotion of Science, and by the Premier Research Institute for Ultrahigh-pressure Sciences (PRIUS) joint research program carried out at the Geodynamics Research Center, Ehime University. This research was supported by NSF Grants EAR-1452344 (SDJ), EAR-0847951 (CRB), the Carnegie/DOE Alliance Center (CDAC), the David and Lucile Packard Foundation, and by the Alexander von Humboldt Foundation.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.pepi.2015.03.010.


