Water partitioning between bridgmanite and postperovskite in the lowermost mantle

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Abstract

The lowermost mantle appears to contain geochemically primitive reservoirs of volatile components including water, as evidenced by certain ocean island basalts [17]. We used *ab-initio* lattice dynamics to calculate the water partition coefficient between bridgmanite and postperovskite using quasi-harmonic free energies to determine how water is distributed between nominally anhydrous minerals in the D'' region. In the absence of aluminum, hydrogen was incorporated into both phases by a simple substitution of $\text{Mg}^{2+} \Leftrightarrow 2\text{H}^+$, and we found that water favors bridgmanite over postperovskite by a factor of about 5:1 at conditions where an average mantle geotherm intersects the phase boundary. In the Al-bearing system, hydrogen and aluminum were coupled as $\text{Si}^{4+} \Leftrightarrow \text{Al}^{3+} + \text{H}^+$ defects into both phases, and we found that water favors postperovskite over bridgmanite in the Al-bearing system by a factor of about 3:1 at ambient mantle conditions, and by about 8:1 at colder slab conditions. Our results indicate that aluminum controls the partitioning of water between bridgmanite and postperovskite, and that aluminous postperovskite may be a potential host for primordial water in the lowermost region of the mantle. The strong partitioning of water into aluminous

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postperovskite over bridgmanite provides a potential mechanism for dehydration melting in the lowermost mantle that could be a source for ocean island basalts in regions of upwelling.

8 *Keywords:* Nominally anhydrous minerals, Water partitioning, Density
9 functional theory

10 **1. Introduction**

11 A comprehensive geochemical and geophysical description of the evolu-
12 tion and state of the lowermost mantle, or D'' region, remains a challenging
13 problem more than 60 years after its discovery [8]. The D'' region is complex
14 but is typically characterized by anti-correlated bulk and shear wave veloci-
15 ties, laterally varying thickness between 0 to >300 km, complicated seismic
16 anisotropy structure, and large regions of generally low shear wave velocities
17 [18, 29, 10]. These features have been attributed to chemical heterogene-
18 ity [49], phase transformations [31], and partial melting [12]. More recently,
19 geochemical and geodynamical evidence suggests the existence of primor-
20 dial un-degassed, volatile-rich reservoirs in the lowermost mantle [17, 50, 15].
21 Yet after more than a decade of work on the bridgmanite-postperovskite
22 (brg-ppv) phase transition, the distribution of volatile elements and melt
23 generation in the lowermost mantle remains poorly understood [13, 11].

24 The effects of major element chemistry on the brg-ppv transition to date
25 have focused mostly on iron and aluminum. For pure MgSiO_3 the brg-ppv
26 phase transformation occurs at approximately 125 GPa and 2500 K, cor-
27 responding to about 2700 km depth; about 300 km above the core-mantle
28 boundary (CMB) along a mantle geotherm. The Clapeyron slope of the

29 phase boundary has been estimated to be 4-14 MPa/K, and while well de-
 30 fined only for univariant systems, the effective Clapeyron slope of the Al
 31 and Fe-bearing systems indicates that it is relatively insensitive to composi-
 32 tion [31, 10, 48, 34]. However, for expected mantle compositions including
 33 aluminum, there exists a two-phase region of coexisting brg and ppv which
 34 reduces the velocity gradient and slightly decreases the transition depth in
 35 the case of aluminum, but not appreciably in the case of iron [1, 44, 20].
 36 Experiments on iron- and aluminum-bearing compositions indicate that a
 37 pyrolitic D'' might not contain any ppv, while for MORB compositions the
 38 transition depth may lie several hundred kilometers above the CMB [16].

39 Despite the focus on the effects of major element composition, the influ-
 40 ence of geophysically important trace impurities such as water on the brg-
 41 ppv transition have not been investigated. Hernández et al. [19] estimated
 42 a ringwoodite:bridgmanite (rw:brg) water partition coefficient of 1:0.1 at 24
 43 GPa and 1500 K via *ab-initio* density functional theory (DFT) techniques.
 44 Panero et al. [37] synthesized bridgmanite in the diamond-anvil cell from
 45 naturally-occurring enstatite containing 2065 ppm H₂O at 25-65 GPa and
 46 1600-2000 K, finding that likely no more than 10 ppm H₂O entered the
 47 brg phase. Complementary first-principles calculations under static (0 K)
 48 conditions indicated that Mg-bridgmanite can accommodate a maximum of
 49 30-40 ppm H₂O at conditions throughout the lower mantle. Although no
 50 experimental work has been performed on water partitioning between ppv
 51 and brg, Townsend et al. [42] described a hydrous post-perovskite structure
 52 (hppv) using DFT methods stable under D'' pressures. The hppv structure,
 53 charge balanced by Mg-site vacancies (Mg_{1-x}H_{2x}SiO₃), exhibits bulk and

54 shear moduli that are reduced by about 7-10 GPa/wt% H₂O compared with
55 dry ppv at D'' pressures.

56 To investigate the water partition coefficient between brg and ppv in
57 the lowermost mantle, we used first-principles calculations of total energy
58 and *ab-initio* lattice dynamics simulations to compute the quasi-harmonic
59 free energies of for two varieties of hydrogen defects, with and without alu-
60 minum, in bridgmanite and postperovskite. For aluminum-bearing hydrous
61 compositions we find that ppv is stabilized relative to brg under static con-
62 ditions, and that the water partition coefficient of ppv relative to brg is 3.2:1
63 along an ambient mantle geotherm, and 8.1:1 along a slab geotherm. Our re-
64 sults demonstrate that aluminous postperovskite may store significantly more
65 water than aluminous bridgmanite, and suggest that D'' may host primor-
66 dial water even in the absence of dense-hydrous-magnesium-silicates such as
67 phase H [33]. The bulk sound velocity impedance contrast across the brg-ppv
68 transition and the ppv velocity gradient are more sensitive to the presence
69 of water than the velocities themselves, which suggests that velocity pertur-
70 bations alone may not be sufficient to investigate the hydration state of the
71 lower mantle. In regions of the lowermost mantle where upwelling primordial
72 hydrous postperovskite transforms to bridgmanite, water would be liberated
73 due to the large difference in partitioning between these phases, and might
74 generate melts at the base of the mantle by dehydration reactions, analogous
75 to dehydration melting reactions across the 410- and 660-km discontinuities
76 of the mantle transition zone [5, 35, 21, 39].

2. Methods

2.1. Partition coefficient

We computed the water partition coefficient between brg and ppv in two systems. In the aluminum-free system hydrogen is incorporated into both phases by $\text{Mg}^{2+} \Leftrightarrow 2\text{H}^+$ (hereafter called Mg-2H mechanism). In the aluminum-bearing system hydrogen is incorporated into both phases by a coupled substitution $\text{Si}^{4+} \Leftrightarrow \text{Al}^{3+} + \text{H}^+$ (hereafter called Si-AlH mechanism). Following the procedure of Hernández et al. [19], the water partition coefficient D between brg and ppv for a particular defect type Y is controlled by the Gibbs free-energy of formation of the defect in each phase (see Appendix 1):

$${}^Y D_{brg}^{ppv} = \frac{e^{G_{brg}^f/k_B T} + 1}{e^{G_{ppv}^f/k_B T} + 1} \approx e^{\Delta G_{brg-ppv}^f/k_B T} \quad (1)$$

where ${}^Y D_{brg}^{ppv}$ is the partition coefficient of defect Y in ppv relative to brg, G^f is the Gibbs free-energy of formation of a Y defect in brg or ppv, k_B and T are Boltzmann's constant and temperature, respectively. Therefore, in order to compute the partition coefficient, the Gibbs free energies for all phases with and without defects is required. The above formulation assumes that defects are partitioning between two solid phases in the absence of any fluids. As with previous work (cf. [19]), the results do not represent water storage capacity which is defined as the amount of water in a nominally anhydrous mineral in equilibrium with a hydrous melt [26].

2.2. Computational Technique

First-principles calculations of total energy for each structure were carried out with the Quantum ESPRESSO package, an implementation of density

functional theory with plane wave basis sets [22, 27, 14]. The exchange-correlation energy was computed using the Perdew-Ernzerhof-Burke generalized gradient approximation [38], and the k-space mesh was generated by the Monkhorst-Pack scheme [30]. Norm-conserving pseudopotentials were used to describe H, O, and Si [43], and the Mg pseudopotential was generated by the method of von Barth and Car [4]. These pseudopotentials have been used in numerous investigations of both hydrous and anhydrous mantle silicates [25, 48, 45, 33, 42]. For all models a plane wave energy cutoff was set at 100 Ry, and a 2x2x2 k-space mesh was used, and were tested for convergence. For brg we designed a 2x2x1 supercell, and for ppv we designed a 4x1x1 supercell, each containing 80 atoms in the defect free models. Each structure was relaxed at 0, 30, 60, 90, 100, 110, 120, 130, and 150 GPa, and were considered relaxed when the average force per atom was less than 10^{-4} eV/atom. In order to adequately sample the vibrational properties throughout reciprocal space, phonon dispersion calculations were performed on the relaxed structures using a 2x2x2 $\mathbf{q}$ -point grid and the resulting force constant matrix was used to interpolate the phonon frequencies on a fine mesh of 260 $\mathbf{q}$ -points [3]. Increasing the number of $\mathbf{q}$ -points did not significantly affect the free energies of the structures.

2.3. Quasi-harmonic free-energy calculations

The Gibbs free-energy G at pressure P and temperature T can be expressed as a minimization problem in the volume V [41]:

$$G(P, T) = \min_V \{U^{static}(V) + F^{vib}(T; V) + PV\} \quad (2)$$

122 where $U^{static}(V)$ is the energy of the static lattice at volume V , and under
 123 the quasi-harmonic approximation the vibrational contribution to the free
 124 energy $F^{vib}(V, T)$ is given by:

$$F^{vib}(T; V) = \sum_{s, \mathbf{q}} \frac{1}{2} \hbar \omega_s(\mathbf{q}; V) + k_B T \ln \left(1 - \exp \left(-\frac{\hbar \omega_s(\mathbf{q}; V)}{k_B T} \right) \right) \quad (3)$$

125 where the sum runs over all phonon branches, s , and all points in the Brillouin
 126 zone, $\mathbf{q}$, and $\omega_s(\mathbf{q}; V)$ is the frequency of the s^{th} phonon at $\mathbf{q}$ at volume V , and
 127 $\hbar$ is the reduced Planck's constant. To account for the volume dependence
 128 of each phonon frequency the set of phonon dispersion curves was used to
 129 compute the mode Grüneisen parameters:

$$\gamma_s(\mathbf{q}; V) = -\frac{V}{\omega_s(\mathbf{q}; V)} \frac{d\omega_s(\mathbf{q}; V)}{dV} \quad (4)$$

130 where the derivative is evaluated from finite differences.

131 In practice, eq. (2) is evaluated for each model by the following scheme:
 132 First, the $\{\gamma_s(\mathbf{q}; V)\}$'s were computed according to eq. (4). Then for a given
 133 pressure and temperature $G(P, T; V)$ was constructed from a set of isother-
 134 mal calculations at several volumes in which the γ 's were used to adjust
 135 the frequencies. Finally, the resulting V, G data were fit with an isothermal
 136 equation of state. For the static EOS and the isothermal Gibbs free energy
 137 we used the 3^{rd} order Birch-Murnaghan isothermal equation of state:

$$U(V) = U_0 + \frac{9K_{0T}V_{0T}}{16} \left\{ K'_{0T} \left[\left(\frac{V_{0T}}{V} \right)^{2/3} - 1 \right]^3 + \left[\left(\frac{V_{0T}}{V} \right)^{2/3} - 1 \right]^2 \left[6 - 4 \left(\frac{V_{0T}}{V} \right)^{2/3} \right] \right\} \quad (5)$$

138 where U_0 is the energy at volume V_{0T} , K_{0T} is the zero-pressure bulk modulus,
 139 and K'_{0T} is the zero-pressure pressure derivative of the bulk modulus, all at
 140 constant temperature T .

141 3. Results

142 3.1. Defect structures

143 The crystal structure models used in this study are shown in fig. 1, and
144 are provided in the supplementary materials. We considered two types of
145 charge-balanced hydrogen defects in both bridgmanite and postperovskite.
146 In the first set of models (hbrg/hppv) we used the Mg-2H defect (1.14 wt.%
147 water), following Townsend et al. [42]. In the second set of models (Al-
148 hbrg/Al-hppv) we used the Si-AlH defect (0.56 wt.% water). Our hbrg defect
149 structure is somewhat different than the one given in Hernández et al. [19].

150 The hydrogen bond geometry for all the defect structures at 120 GPa is
151 given in table 1. Over the entire pressure range covered in this study (0-150
152 GPa), the O-H bonds for the Al-bearing defect structures of both phases
153 are relatively longer than for the Al-free defects. Upon compression from 0
154 to 120 GPa the O-H bond lengthens for the Al-bearing defect structures by
155 approximately 0.034 Å, or 2%, for both structures, and for the Al-free defect
156 structures the O-H bonds lengthen by approximately 0.009 Å, or 1%. In Al-
157 free hbrg and hppv two hydrogen atoms share a magnesium vacancy, while in
158 Al-hbrg and Al-hppv the hydrogen occupies an interstitial site. Referring to
159 table 1, the hydrogen bonds in Al-free hbrg and hppv are highly asymmetric
160 and non-linear, with a hydrogen bond angle of around 115 degrees. The
161 hydrogen bond in Al-free hppv is slightly stronger, with a hydrogen-bond
162 distance $d(\text{O} \dots \text{O})$ about 4% shorter than in Al-free hbrg. In the Al-bearing
163 system, the hydrogen bonds are considerably more symmetric and linear,
164 with hydrogen bond angles close to 180 degrees. The hydrogen bond in Al-
165 hppv is the strongest among all defect models studied here, being about 3%

Table 1: Hydrogen bond geometries at 120 GPa for bridgmanite and postperovskite models used in this study.

Defect structure	$d(\text{OH})$ Å	$d(\text{O}\dots\text{O})$ Å	$d(\text{O}\dots\text{H})$ Å	H-bond angle deg.
hbrg	0.996	2.397	1.800	114.94
hppv	0.993	2.307	1.708	114.73
Al-hbrg	1.073	2.330	1.258	177.89
Al-hppv	1.049	2.269	1.221	176.97

166 shorter than the hydrogen bond in Al-hbrg and 5% shorter than the hydrogen
167 bond in Al-free hbrg.

Figure 1: Crystal structures used in this study. (top left) Al-free bridgmanite, (top middle) Al-free hydrous bridgmanite, (top right) Al-bearing hydrous bridgmanite, (bottom left) Al-free post-perovskite, (bottom middle) Al-free hydrous post-perovskite, and (bottom right) Al-bearing hydrous postperovskite. In all structures orange, dark blue, light blue, red, and black spheres represent magnesium, silicon, aluminum, oxygen, and hydrogen, respectively.

168 The effect of the defects on the static enthalpy and the defect formation
 169 enthalpies for both defects at 0 K are shown in fig. 2. We find that Si-
 170 AlH defects favor the ppv phase under static conditions, in agreement with
 171 previous DFT calculations [1], while Mg-2H defects favor brg over ppv. The
 172 preference for Si-AlH defects in the ppv phase may be due to the difference in

173 the bonding environment of hydrogen discussed above rather than aluminum
 174 because in ppv and brg at 120 GPa the polyhedral volume of AlO_6 is about
 175 3% larger in ppv compared to brg, consistent with [46]. If we assume the
 176 brg-ppv phase boundary at 0 K depends linearly on the defect concentration,
 177 then the Mg-2H defects increase the transition by 8.6 GPa per wt.% H_2O ,
 178 whereas for the Si-AlH defects the transition decreases by 11.8 GPa per wt.%
 179 H_2O . From the static enthalpies alone we predict that water should partition
 180 into brg over ppv in the absence of aluminum, and into ppv over brg in the
 181 presence of aluminum.

Figure 2: Left: Difference in enthalpy for pure ppv-brg (black), Mg-2H defect models (hppv-hbrg) (red), and Si-AlH defect models (Al-hppv-Al-hbrg) (blue). The dry ppv-brg transition pressure is 104.4 GPa, the aluminum-free hppv-hbrg transition pressure is 114.2 GPa, and the Al-hppv-Al-hbrg transition pressure is 97.8 GPa. Right: Difference in defect formation enthalpy for Al-free (red) and Al-bearing (blue) hydrogen defects.

Table 2: 3rd order Birch-Murnaghan equation of state parameters used in this study.

Structure	K_0	K'_0	V_0	U_0
	GPa	-	Å ³ /supercell	eV/supercell
brg	246	3.80	662.087	-23524.565
ppv	216	4.13	662.537	-23520.775
hbrg	238	3.81	662.812	-23523.679
hppv	205	4.17	665.543	-23520.282
Al-hbrg	239	3.82	670.251	-23471.435
Al-hppv	207	4.19	670.407	-23467.653

182 3.2. Equations of state and free energy calculations

183 The static volume-energy curves were used to fit isothermal 3rd order
184 Birch-Murnaghan equations of state (eq. (5)) for each model with a non-linear
185 least squares algorithm and the EOS parameters used for each structure are
186 shown in table 2. Consistent with other nominally anhydrous minerals such
187 as wadsleyite and ringwoodite [9], hydrogen lowers the zero-pressure bulk
188 modulus, increases the zero-pressure volume, and we find a weak dependence
189 of K'_0 on water concentration for all hydrous structures. For both brg and ppv
190 structures the Mg-2H defect models are more compressible than those with
191 Si-AlH defects, consistent with the fact that the Mg-2H defect mechanism
192 features hydrogen occupying an Mg-vacancy.

193 We calculated the phase diagram for dry brg and ppv from the quasi-
194 harmonic free energy calculations, presented in fig. 3, as the first step towards
195 computing the partition coefficients. At 125 GPa and 2880 K, we predict a
196 clapeyron slope of 7.6 MPa/K, in good agreement with both experimental

197 and computational work [36, 34, 48, 31, 20]. Because the QHA assumes
198 the phonon frequencies are temperature independent, calculations at high
199 temperature are not accurate. However, previous studies of QHA energies of
200 brg and ppv indicate that the QHA is valid for brg and ppv in the lowermost
201 mantle [47].

Figure 3: Calculated phase diagram of MgSiO_3 . Filled and open points represent experimental observation of brg and ppv, respectively [36, 31]. The thin black dashed line shows the limit of the validity of our QHA calculations. Thin colored dashed lines represent phase boundaries from previous first-principles calculations using both the LDA and GGA [48, 34]. The vertical solid black line denotes the pressure at the core mantle boundary (CMB).

202 3.3. Partition coefficients

203 From the brg-ppv phase diagram we compute the partition coefficients
204 between hppv-hbrg and Al-hppv-Al-hbrg in fig. 4. For the Al-free (Mg-
205 2H) system the water partition coefficient between hppv and hbrg (fig. 4
206 top left) is less than one at every point along the phase boundary, indicat-
207 ing that in equilibrium there are more Mg-2H defects in bridgmanite than
208 postperovskite. Additionally, partitioning along mantle and slab geotherms
209 are not significantly different. At 121.5 GPa and 2400 K, where the mantle
210 geotherm intersects the phase boundary, the partition coefficient is approx-
211 imately 0.2:1, while at 113.5 GPa and 1370 K, where the slab geotherm in-
212 tersects the phase boundary, the partition coefficient is approximately 0.03:1
213 (fig. 4 top right). In contrast, in the Al-bearing (Si-AlH) system the water
214 partition coefficient between ppv and brg is greater than one everywhere,
215 especially at low temperatures (or, equivalently, if traveling along the phase
216 boundary, low pressure) (fig. 4 bottom left). The partitioning of Si-AlH de-
217 fects is more sensitive to temperature and less sensitive to pressure, which
218 results in more than a factor of two difference in partitioning along ambient
219 mantle and slab geotherms. At 121.5 GPa and 2400 K, where the mantle
220 geotherm intersects the phase boundary, the Al-hppv:Al-hbrg partition coef-
221 ficient is approximately 3.2:1, while at 113.5 GPa and 1370 K, where the slab
222 geotherm intersects the phase boundary, the partition coefficient is approxi-
223 mately 8.1:1 (fig. 4 bottom right). By construction, the partition coefficient
224 requires that brg-ppv are in equilibrium which is true for each pressure only
225 at a single temperature because the brg-ppv phase boundary is univariant for
226 pure MgSiO_3 . Nevertheless, the effect of temperature on the free energy is

227 relatively small compared to the effect of pressure and so the partition coeffi-
228 cient should be valid for small thermal variations about the phase boundary
229 [19]. Therefore the map view of the partition coefficient (fig. 4 left column) is
230 not valid far from the brg-ppv phase boundary, but in both cases it illustrates
231 the general feature that the partition coefficients for both defects are more
232 sensitive to temperature than pressure because the formation energies of the
233 defects are nearly constant as a function of pressure.

234 4. Discussion

235 Our results suggest that aluminum affects the qualitative behavior of
236 water partitioning between brg and ppv. We estimate that for the hbrg-hppv
237 system the H_2O partition coefficient is 0.20:1 at 121.5 GPa and 2400 K, where
238 the mantle geotherm intersects the phase boundary, and 0.03 at 113.5 GPa
239 and 1370 K, where the slab geotherm intersects the phase boundary. However
240 for the Al-hppv-Al-hbrg system the H_2O partition coefficient is 3.2:1 at 121.5
241 GPa and 2400 K, where the mantle geotherm intersects the phase boundary,
242 and 8.1:1 at 113.5 GPa and 1370 K, where the slab geotherm intersects the
243 phase boundary.

244 The water storage capacity of bridgmanite and partitioning of water be-
245 tween bridgmanite and other minerals has been investigated in several pre-
246 vious studies. Bolfan-Casanova et al. [6] found in the Fe and Al-bearing
247 system, no more than a few ppm of H_2O was incorporated into bridgman-
248 ite with up to about 75 ppm H_2O in ferropericlase. Murakami et al. [32]
249 found in bridgmanite synthesized from natural hornblende, that bridgmanite
250 contained 0.2 wt.% water and 6 wt.% Al, however, their FTIR spectra did

251 not resemble OH in bridgmanite and displayed a strong 3700 cm^{-1} peak due
252 to brucite, indicative of a hydrous melt phase [39]. Inoue et al. [24] mea-
253 sured the partition coefficient of water in ringwoodite relative to bridgmanite
254 finding 15:1, and estimate 0.1 wt.% water in bridgmanite synthesized from a
255 starting composition of Fo80 + 16 wt.% water. Hernández et al. [19], using
256 first-principles calculations, computed the H_2O partition coefficient between
257 pure MgSi_2O_4 ringwoodite, MgO periclase, and MgSiO_3 bridgmanite, and
258 found a ringwoodite-bridgmanite H_2O partition coefficient of about 10:1.
259 Panero et al. [37] synthesized bridgmanite from a natural Fe-bearing (0.1
260 wt% Al) hydrous enstatite and found a maximum of 220 ppm water, and
261 complementary first-principles calculations under static conditions confirm a
262 low water partition coefficient for Fe-bearing bridgmanite.

263 4.1. Prospects for seismic detectability

264 To illustrate the influence of hydration on the brg-ppv transition on
 265 seismic parameters in D'', fig. 5 shows the adiabatic bulk sound velocity
 266 ($V_{\Phi} = \sqrt{K_S/\rho}$) for a hypothetical scenario in which we partition 1 wt.%
 267 water between ppv and brg along a 1600 K isentrope. For a dry composition,
 268 a drop in bulk sound velocity of around -0.09 km/s (-0.08%) is expected
 269 across the brg-ppv phase transition. For a hypothetical hydrous composi-
 270 tion assuming 1 wt.% water and a ppv:brg water partition coefficient of 3.2:1
 271 (i.e. assuming Si-AlH defect partitioning), the change in V_{Φ} is about -0.06
 272 km/s (-0.05%), or about half that of the dry scenario. At D'' pressures it
 273 is perhaps unsurprising that the effect of hydration on the velocity is small,
 274 however we find that the average velocity gradient $(dV_{\Phi}/dP)_S$ of Al-hppv
 275 increases with water content. Additionally, the seismic impedance contrast
 276 ($\rho_{brg}V_{\Phi,brg} - \rho_{ppv}V_{\Phi,ppv}$) in this hydrous scenario is reduced by approximately
 277 50% of that in the dry scenario. In combination, these two observables might
 278 provide a way to probe the hydration state of the lower mantle, as has re-
 279 cently been proposed for the transition zone [40].

280 4.2. Limitations

281 There are several limitations to our approach which highlight the need
 282 for future experiments and simulations. Most importantly, the partition co-
 283 efficient depends on the static and vibrational energies for a particular defect
 284 configuration. Figure 2 indicates that at D'' pressures the aluminum-free
 285 hydrous defect formation enthalpy is very large and positive, and that the
 286 aluminum-bearing hydrous defect formation enthalpy is relatively small and
 287 negative. While the exact value of the partition coefficient will change for

different defect configurations, the overall result, that water partitions preferentially into postperovskite in the presence of aluminum, and preferentially into bridgmanite in the absence of aluminum, is likely robust. Indeed, the stabilization of Al-hppv relative to Al-hbrg was first noticed under static conditions by Akber-Knutson et al. [1]. It is important to point out that the water-partitioning estimates presented here require all of the Al to be in the form of Si-AlH defects, and as a result may overestimate the partition coefficient. Further, in this study our partition coefficient results assume only a single type of hydrogen defect within each phase, whereas in real crystals there are likely several coexisting varieties of hydrous defects, which should be explored in future studies.

Another important limitation is that we have not accounted for the influence of iron or other minerals on the partitioning. The spin-state of iron in both brg and ppv are still areas of active research, but previous studies indicated that for both brg and ppv iron may adopt an intermediate spin configuration [23]. As both the valence and spin-state of iron affect its ionic radius, the presence of iron will likely have an influence on the partition coefficients. Ferropericlase (fp) coexists with brg and ppv throughout D'' , and while not a significant host for water itself, would affect the iron partitioning between brg and ppv, and therefore may also affect water partitioning between other phases.[2].

4.3. Summary

In summary, our results indicate that aluminous postperovskite has the potential to hold significantly more water than bridgmanite. Recent geochemical measurements suggest the presence of a long-lived primordial reser-

313 voir in the deep lower mantle [17]. If geochemically primordial and relatively
 314 volatile-rich material exists in D'' , our results suggest that aluminous ppv
 315 may be a host for such primordial water. In the past, melting at the base of
 316 the mantle has been proposed to be the last vestiges of a basal magma ocean
 317 [28]. However, in regions where primordial hydrous ppv is swept by man-
 318 tle convection currents through the ppv-brg phase boundary and transforms
 319 to brg, the large contrast in the partition coefficient may be an additional
 320 mechanism for generating melts via dehydration melting.

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Figure 4: Top left: Map of the H₂O partition coefficient of ppv relative to brg for the Mg-2H defect model ($^H D_{brg}^{ppv}$). Top right: Partition coefficients at the brg-ppv coexistence pressures for the mantle (red) and slab (blue). Bottom left: Map of the H₂O partition coefficient of ppv relative to brg for the Si-AlH defect ($^{AlH} D_{brg}^{ppv}$). Bottom right: Partition coefficients at the brg-ppv coexistence pressures for the mantle (red) and slab (blue). In both maps the solid black line is the phase boundary between pure brg-ppv shown in fig. 3, the dotted black lines are mantle and slab adiabats [7, 33], and the bright red and blue lines mark the P, T paths of the 1d slices shown at right.

Figure 5: Adiabatic bulk sound velocity along a self-consistently calculated 1600 K isentrope, for which the brg-ppv transition occurs at 122 GPa and 2516 K. The black curve shows the bulk sound velocity for the dry system, and the blue curve shows the bulk sound velocity for an aluminous hydrous system with an arbitrarily chosen 1 wt.% water partitioned between ppv and brg assuming a partition coefficient of 3.2:1.

338 Appendix A. Derivation of the partition coefficient

339 The equilibrium distribution of a dilute component between two otherwise
 340 pure bulk solids is determined by the Gibbs free energies of the pure and
 341 dilute phases. This derivation draws from that given in [19]. Given a collec-
 342 tion of N unit cells of two pure phases α and β , and n_α unit cells of α which
 343 contains a single defect, and similarly for β , where $N \gg n_\alpha, n_\beta$, the Gibbs
 344 free energy G of a mixture of pure and defective unit cells of phase α can be
 345 written as:

$$G_\alpha(n_\alpha) = G_\alpha^0(n_\alpha) - TS_\alpha^{conf}(n_\alpha) \quad (\text{A.1})$$

346 where T is temperature, and S is entropy. The leading term is just the Gibbs
 347 free energy of N unit cells composed of n_α defect cells and $N - n_\alpha$ pure unit
 348 cells:

$$G_\alpha^0 = (N - n_\alpha)F_\alpha^{pure} + n_\alpha F_\alpha^{defect} + n_\alpha P\Delta V_\alpha$$

349 where F is the Helmholtz free energy, P is the pressure, and V is the volume.
 350 The configurational entropy, S^{conf} is:

$$S^{conf}(n_\alpha) = k_B \ln \left(\frac{N_x!}{(N_x - n_\alpha)!n_\alpha!} \right)$$

351 Where N_x is the number of possible crystallographic sites of the defect, and
 352 n_a is the number of defects. To see the effect of n_α on the total energy we
 353 compute the partial molar derivative of eq. (A.1):

$$\frac{\partial G_\alpha(n_\alpha)}{\partial n_\alpha} = -F_\alpha^{pure} + F_\alpha^{defect} - T \frac{\partial S_\alpha^{conf}(n_\alpha)}{\partial n_\alpha} + P\Delta V_\alpha = G_\alpha^f - T \frac{\partial S_\alpha^{conf}(n_\alpha)}{\partial n_\alpha}$$

354 where $G_\alpha^f = G_\alpha^{defect} - G_\alpha^{pure}$, is the Gibbs free energy of formation. The
 355 partial molar derivative of the configurational entropy is:

$$\frac{\partial S_\alpha^{conf}}{\partial n_\alpha} = k_B \ln \left(\frac{N_x - n_\alpha}{n_\alpha} \right)$$

356 Repeating the same procedure for β yields the pair of equations:

$$\begin{aligned} \frac{\partial G_\alpha}{\partial n_\alpha} &= G_\alpha^f - k_B T \ln \left(\frac{N_x - n_\alpha}{n_\alpha} \right) \\ \frac{\partial G_\beta}{\partial n_\beta} &= G_\beta^f - k_B T \ln \left(\frac{N_x - n_\beta}{n_\beta} \right) \end{aligned}$$

Setting both derivatives equal to zero at equilibrium:

$$\begin{aligned} \frac{G_\alpha^f}{k_B T} &= \ln \left(\frac{N_x - n_\alpha}{n_\alpha} \right) \implies e^{G_\alpha^f/k_B T} = \frac{N_x - n_\alpha}{n_\alpha} \\ \frac{G_\beta^f}{k_B T} &= \ln \left(\frac{N_x - n_\beta}{n_\beta} \right) \implies e^{G_\beta^f/k_B T} = \frac{N_x - n_\beta}{n_\beta} \end{aligned}$$

Solving for n_α and n_β we obtain the pair of equations:

$$\begin{aligned} n_\alpha &= \frac{N_x}{e^{G_\alpha^f/k_B T} + 1} \\ n_\beta &= \frac{N_x}{e^{G_\beta^f/k_B T} + 1} \end{aligned}$$

358 Finally, the partition coefficient (D_β^α), is just the ratio of the number of
359 defects in the two phases:

$$D_\beta^\alpha = \frac{n_\alpha}{n_\beta} = \frac{e^{G_\beta^f/k_B T} + 1}{e^{G_\alpha^f/k_B T} + 1} \approx e^{\Delta G_{\beta-\alpha}^f/k_B T} \quad (\text{A.2})$$

360 The above derivation assumes equal amounts N of α and β , the only con-
361 ditions under which such can coexist is along the phase boundary. As a
362 result, it should be understood that this formulation is accurate only along
363 the phase boundary and only for dilute concentrations.

An alternative derivation works directly from the chemical potentials. For two components – 1, the dilute solute, and 2, the solvent – and for two phases – α and β , each composed of components 1 and 2 – the conditions of exact

equilibrium are:

$$\begin{aligned}\mu_1^\alpha(P, T, X_1^\alpha) &= \mu_1^\beta(P, T, X_1^\beta) \\ \mu_2^\alpha(P, T, X_2^\alpha) &= \mu_2^\beta(P, T, X_2^\beta)\end{aligned}$$

where μ_1^α is the chemical potential of component 1 in phase α , and similarly for the other terms. Assuming an ideal solution, the μ 's take the following form:

$$\begin{aligned}{}^0\mu_1^\alpha(P, T) + k_B T \ln X_1^\alpha &= {}^0\mu_1^\beta(P, T) + k_B T \ln X_1^\beta \\ {}^0\mu_2^\alpha(P, T) + k_B T \ln (1 - X_1^\alpha) &= {}^0\mu_2^\beta(P, T) + k_B T \ln (1 - X_1^\beta)\end{aligned}$$

with $1 = X_1^\alpha + X_2^\alpha$ and likewise for β , and the superscript 0 denotes the chemical potential for the pure end-member. Rearranging for X_1 in both phases we obtain:

$$\begin{aligned}X_1^\alpha &= X_1^\beta e^{\Delta^0\mu_1^{\beta-\alpha}/k_B T} \\ X_1^\beta &= \frac{1 - e^{\Delta^0\mu_2^{\beta-\alpha}/k_B T}}{e^{\Delta^0\mu_1^{\beta-\alpha}/k_B T} - e^{\Delta^0\mu_2^{\beta-\alpha}/k_B T}}\end{aligned}\tag{A.3}$$

364 where $\Delta^0\mu_1^{\beta-\alpha}$ is the difference of the chemical potentials of the two end-
365 members. Finally, the partition coefficient is just the ratio of the concentra-
366 tions of the dilute component 1 in both phases:

$${}^1D_\beta^\alpha = \frac{X_1^\alpha}{X_1^\beta} = e^{\Delta^0\mu_1^{\beta-\alpha}/k_B T}$$

To show these two approaches are equivalent, we make the simplification $X_1 = X$ and $X_2 = 1 - X$, and denote by $\tilde{G}$ the free energy per cell, so that the Gibbs free energies of formation are:

$$\begin{aligned}\tilde{G}_{defect}^\alpha - \tilde{G}^\alpha &= (1 - X)^0\mu_2^\alpha + X^0\mu_1^\alpha + k_B T (X \ln(X) + (1 - X) \ln(1 - X)) - {}^0\mu_2^\alpha \\ \tilde{G}_{defect}^\beta - \tilde{G}^\beta &= (1 - X)^0\mu_2^\beta + X^0\mu_1^\beta + k_B T (X \ln(X) + (1 - X) \ln(1 - X)) - {}^0\mu_2^\beta\end{aligned}$$

367 The differential Gibbs free energy of formation is the difference of the above:

$$\Delta\tilde{G}^f = \tilde{G}_{defect}^\alpha - \tilde{G}^\alpha - (\tilde{G}_{defect}^\beta - \tilde{G}^\beta) = X \left({}^0\mu_1^\alpha - {}^0\mu_2^\alpha - ({}^0\mu_1^\beta - {}^0\mu_2^\beta) \right)$$

368 But, on the phase boundary ${}^0\mu_2^\alpha \approx {}^0\mu_2^\beta$ if the defects are dilute, which leaves:

$$e^{\Delta\tilde{G}^f/k_B T} = e^{X\Delta{}^0\mu_1^{\alpha-\beta}/k_B T}$$

369 Which is equivalent to the result of Hernández et al. [19] in the case of equal
 370 numbers of equivalent positions in each structure. However, if the number
 371 of equivalent positions is different in the two phases, then the above must
 372 be modified to take into account mixing on sites. Therefore, the partition
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