

Revision 1

1 **Calculation of the energetics of water incorporation in majorite garnet**

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7 **Abstract**

8 Interpretation of lateral variations in upper mantle seismic wave speeds requires
9 constraints on the relationship between elasticity and water concentration at high-pressure for all
10 major mantle minerals, including the garnet component. We have calculated the structure and
11 energetics of charge-balanced hydrogen substitution into tetragonal MgSiO₃ majorite up to $P =$
12 25 GPa using both classical atomistic simulations and complementary first-principles
13 calculations. At the pressure conditions of Earth's transition zone, hydroxyl groups are predicted
14 to be bound to Si vacancies as the hydrogarnet defect, $[V_{\text{Si}} + 4\text{OH}_0]^X$, at the Si2 tetrahedral site
15 or as the $[V_{\text{Mg}} + 2\text{OH}_0]^X$ defect at the octahedral Mg3 site. The hydrogarnet defect is more
16 favorable than the $[V_{\text{Mg}} + 2\text{OH}_0]^X$ defect by 0.8 – 1.4 eV/H at 20 GPa. The presence of 0.4 wt%
17 Al₂O₃ substituted into the octahedral sites further increases the likelihood of the hydrogarnet
18 defect by 2.2-2.4 eV/H relative to the $[V_{\text{Mg}} + 2\text{OH}_0]^X$ defect at the Mg3 site. OH defects affect
19 the seismic ratio, $R = \text{dln}V_s/\text{dln}V_p$, in MgSiO₃ majorite ($\Delta R = 0.9 - 1.2$ at 20 GPa for 1400 ppm
20 wt H₂O) differently than ringwoodite at high pressure, yet may be indistinguishable from the
21 thermal $\text{dln}V_s/\text{dln}V_p$ for ringwoodite. The incorporation of 3.2 wt% Al₂O₃ also decreases $R(\text{H}_2\text{O})$
22 by ~0.2-0.4. Therefore, to accurately estimate transition zone compositional and thermal

23 anomalies, hydrous majorite needs to be considered when interpreting seismic body wave
24 anomalies in the transition zone.

25 **Keywords**

26 Hydrous majorite, Defect mechanisms, Force field, Computer simulation, Density functional
27 theory

28 **Introduction**

29 The amount of water stored in deep crustal and mantle rocks is largely unconstrained, yet
30 may account for a quantity of water comparable to or in excess of the amount contained in the
31 present oceans (Hirschmann 2006). Water has a first-order effect on the compressibility and
32 deformation of the crust and mantle (e.g., Smyth et al. 2004; Xu et al. 2013) in addition to
33 melting temperature, electrical and thermal conductivity (e.g., Hirschmann 2006; Panero et al.
34 2013; Thomas et al. 2012). Since water is incorporated into the nominally anhydrous mineral
35 phases of Earth's mantle in the form of H defects (e.g., Wright 2006), a clear understanding of
36 the atomic scale behavior and substitution mechanism of hydrogen in high-pressure silicates is
37 critical to our knowledge of mantle processes.

38 Majorite, $(\text{Mg,Fe})\text{SiO}_3$, is the high-pressure garnet phase stable at transition-zone depths
39 (410 – 660 km) and is the second most abundant phase after the high-pressure olivine
40 polymorphs, accounting for as much as 40 percent of the rock volume (Frost 2008). The defect-
41 free, tetragonal Mg-endmember garnet, majorite (space group $I4_1/a$), has a structure consisting of
42 3 unique tetrahedral sites (Si1, Si2, and Si3) each linked by corner oxygens to octahedral sites,
43 Mg3 and Si4, and two interstitial distorted dodecahedral sites, Mg1 and Mg2 (Figure 1) (Angel
44 et al. 1989). The 3 tetrahedral sites are distinguished from each other based on the occupancy of
45 the nearest neighbor octahedral sites. The Si1 tetrahedra are linked to Mg3 octahedra, the Si2

46 sites are linked to Si₄ octahedra, and Si₃ tetrahedra are linked to 2 Mg₃ octahedra and 2 Si₄
47 octahedra. The interstitial Mg₁ dodecahedral site is more distorted than the Mg₂ site. There are
48 6 unique oxygen sites (Supplemental Data: Table S1). The O₁ and O₂ sites have the same
49 bonding environment but O₁ is bonded to octahedral Mg and O₂ is bonded to octahedral
50 silicon. The O₃ and O₄ sites are both doubly bonded to the Mg₁ distorted cubic site. Finally, the
51 O₅ and O₆ sites are both involved in 2 cubic environments and 1 tetrahedra but O₆ is bonded to
52 the octahedral Si and O₅ is bonded to the Mg octahedra.

53 The dominant carriers of hydrogen in the transition zone are the high-pressure
54 polymorphs of (Mg,Fe)₂SiO₄ (olivine), wadsleyite and ringwoodite, which can incorporate
55 significant amounts of hydrogen (1-3 wt% H₂O) into their structures (e.g., Kohlstedt et al. 1996;
56 Smyth and Jacobsen 2006). Partitioning experiments in the MgO-SiO₂-H₂O system at transition
57 zone *P-T* conditions show that the olivine polymorphs (wadsleyite and ringwoodite) dissolve ~ 1
58 order of magnitude more than MgSiO₃ (majorite, clinoenstatite, akimotoite) (Bolfan-Casanova et
59 al. 2000) such that $D^{\text{Mg}_2\text{SiO}_4/\text{MgSiO}_3} = \sim 10$. Because the solubility of water in the olivine
60 polymorphs decreases with temperature and the partitioning of water between wadsleyite and
61 ringwoodite may be close to $D^{\text{wad}/\text{ring}} = 1$ at high temperature (Bolfan-Casanova 2005), majorite
62 solubility and partitioning may play an important role throughout the entire thickness of the
63 transition zone. Water solubility in majorite garnet synthesized at transition zone pressures and
64 temperatures can contain up to ~700 ppm wt H₂O (Bolfan-Casanova et al. 2000; Katayama et al.
65 2003), a quantity sufficient to radically change the deformation characteristics of garnet. For a
66 more complete understanding of the implications of OH defects in garnet in the deep mantle,
67 systematic computational studies of hydrogen incorporation into majorite are required.

68 At low pressures, H substitution in andradite garnet ($\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$) takes place via the
69 hydrogarnet defect in which 4 hydrogen atoms charge balance a vacancy ordinarily occupied by
70 a Si atom in the tetrahedral site (Lager et al. 1989). However, the hydrogarnet defect is
71 associated with a volume expansion of the tetrahedral site (e.g., Lager et al. 1989; Purton et al.
72 1992) due to the change in Coulomb forces caused by the Si vacancy and also to accommodate
73 the hydrogen bonded network. This volume expansion should be less energetically favorable at
74 high pressure. Infrared absorption spectra indicate that OH is potentially incorporated into
75 majorite by formation of the hydrogarnet defect (Katayama et al. 2003). However, water
76 concentrations in natural garnet samples brought to the surface from the mantle (Bell and
77 Rossmann 1992a, 1992b) and infrared spectroscopy of both natural garnet (Amthauer and
78 Rossmann 1998; Beran and Libowitzky 2006) and synthetic majorite (Bolfan-Casanova et al.
79 2000) indicate that hydrogen incorporation in majorite may be complex (Williams and Hemley
80 2001). Therefore a systematic investigation of the hydrogen uptake mechanism in majorite is
81 necessary to clarify the situation.

82 Lateral variations in seismic body wave velocities throughout the mantle are caused by
83 temperature and compositional (i.e., water concentration, iron content, partial melting)
84 heterogeneities (Karato 2006). The hydration of transition zone minerals affects the seismic data
85 used to infer high- and low- temperature anomalies and interpretation of mantle plumes and
86 subducted slabs. The seismic ratio, $R = \text{dln}V_s / \text{dln}V_p$ can be used to differentiate between thermal
87 and compositional effects (Karato and Karki 2001). Indeed variations in seismic velocities,
88 expressed as $\text{dln}V_s / \text{dln}V_p$, have been used to suggest a strategy to disentangle the effects of
89 temperature and water content for ringwoodite and wadsleyite (Panero 2010; Li et al. 2011). The
90 temperature and pressure dependence of majorite sound velocities have been established

91 experimentally (Irifune et al. 2008; Sinogeiken and Bass 2002). Constraining the effect of water
92 on majorite elasticity is critical to the accurate interpretation of seismic velocities in Earth's
93 transition zone.

94 By analogy with other H defects in high-pressure silicates, H is likely incorporated into
95 the dodecahedral, octahedral, and tetrahedral sites of the majorite structure. While interstitial
96 hydrogen incorporation is possible in olivine (Balan et al. 2014), it is not likely in the denser
97 garnet structure at high-pressure. Thus, we present a computational investigation of the
98 energetics and associated geophysical properties (P - and S -waves velocities) resulting from
99 hydrogen incorporation in majorite via $[V_{\text{Mg}} + 2\text{OH}_\text{O}]^X$ and $[V_{\text{Si}} + 4\text{OH}_\text{O}]^X$ defects. By comparing
100 the defect energies associated with these different site substitutions of hydrogen, we determine
101 the most favorable hydrogen-defect mechanism. Additionally, we further investigate the
102 influence of aluminum on hydrogen incorporation and wave speeds.

103 **Computational methods**

104 The energies associated with hydrogen and aluminum incorporation in tetragonal
105 majorite garnet (MgSiO_3) were calculated as a function of pressure up to $P = 25$ GPa using
106 classical atomistic simulations based on the Born model of solids, as implemented in the General
107 Utility Lattice Program (GULP) (Gale and Rohl 2003).

108 The initial majorite structure was generated according to the experimental single-crystal
109 structure refinement (Angel et al. 1989). Mg and Si are assumed to be ordered over the 2
110 symmetrically unique octahedral sites based on the low concentration of aluminum ($< \sim 8$ wt%
111 Al_2O_3) and temperature ($T = 0$ K) (Nakatsuka et al. 1999; Vinograd et al. 2006). Majorite lattice
112 energy minimizations were performed using the full body-centered tetragonal unit cell, which
113 consists of 160 atoms.

114 Interatomic potential functions were used to describe the total lattice energy in terms of
115 the atomic positions. We adopt the fractional charges of Vinograd et al. (2006) where ionic
116 charges are scaled by 0.85 to improve transferability with respect to cation-cation distances. The
117 internal lattice energy is dominated by the Coulomb interactions and evaluated using an Ewald
118 summation. We modeled the short-range interactions between closed shell ionic species using a
119 Buckingham potential of the form;

$$120 \quad U_{sr} = \sum_{ij} A_{ij} \exp\left(-\frac{r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6} \quad (1)$$

121 where A , ρ , and C are empirically derived parameters. The sum is over pairs of ions, i and j ($i \neq$
122 j), with a separation distance, r_{ij} . Cutoffs for the Buckingham potentials are 10.0 Å for hydrogen
123 interactions and 12.0 Å for oxygen-oxygen and cation-oxygen interactions. These potentials are
124 tapered to zero over a range of 2.0 Å to ensure smoothness of the potential energy surface (Mei
125 et al. 1991).

126 Due to the partial covalence of the Si-O bond (Pauling 1980), a harmonic angle-bending
127 term was also included:

$$128 \quad U_{ijk} = \frac{1}{2} k_{\theta} (\theta - \theta_0)^2 \quad (2)$$

129 This was applied for both the Si-O and Al-O tetrahedra and octahedra in order to add an energy
130 penalty when there is a deviation from the coordination-dependent equilibrium bond angle.
131 Three-body terms applied to the majorite Si-O and Al-O polyhedra were defined based on
132 bonding between ions, which was defined to be fixed during relaxation, rather than cutoff
133 distances. The three-body contribution to the optimized total energy was confirmed to ensure
134 that the bonding was correctly defined for each system such that no spurious terms were present.
135 A shell model (Dick and Overhauser 1958) was adopted to account for the polarisability of the

136 oxygen anions. The O core-shell interactions are described by spring constants with the
137 functional form:

$$138 \quad U = \frac{1}{2}k_2r^2 + \frac{1}{24}k_4r^4 \quad (3)$$

139 The short-range bonded O-H interaction was described using a Coulomb-subtracted Morse
140 potential (Saul et al. 1985);

$$141 \quad U_r = D_e \left[\left(1 - \exp(-a(r - r_0)) \right)^2 \right] - \frac{q_i q_j}{r} \quad (4)$$

142 where r_0 is the equilibrium bond length, q is the charge of the species, D_e and a are both fitted
143 parameters physically related to the molecular dissociation energy and vibrational frequency.
144 Here the Coulomb term is expressed in atomic units. The Morse potential is cutoff at 1.3 Å,
145 while the Buckingham potential is excluded for the intramolecular interaction within the
146 hydroxyl group.

147 Interatomic potential parameters (Table 1) developed for the anhydrous majorite-pyrope
148 solid solution (Vinograd et al. 2006) were augmented with force field parameters derived by
149 fitting to experimental structural and elastic properties of brucite, $\text{Mg}(\text{OH})_2$, at both 0 GPa and
150 high pressure (Catti et al. 1995; Jiang et al. 2006). Due to the different fractional charge of the
151 hydroxyl oxygen ($\text{O}^{-1.2}$) compared to the non-hydroxyl oxygen ($\text{O}^{-1.7}$), we derived the
152 Buckingham potential parameter, A , by fitting to data for brucite. The two-body potentials for
153 the interaction between the hydroxyl oxygen and both Al and Si were generated from those for
154 the equivalent interaction for non-hydroxyl oxygen using scaling of coefficients (Schröder et al.
155 1992) by 0.709 assuming:

$$156 \quad \frac{A_{Mg-O^{-1.2}}}{A_{Mg-O^{-1.4}}} = \frac{A_{Si-O^{-1.2}}}{A_{Si-O^{-1.4}}} = \frac{A_{Al-O^{-1.2}}}{A_{Al-O^{-1.4}}} \quad (5)$$

157 Validation of the potential model was accomplished through calculation of the structural

158 relaxation, including unit-cell parameters, and elasticity of majorite for pressures between 0 and
159 25 GPa. Additionally, we calculate the structure and elasticity of superhydrous B,
160 $\text{Mg}_{10}\text{Si}_3\text{O}_{14}(\text{OH}_4)$, for pressures between 0 and 25 GPa and the zero-pressure structure and bulk
161 modulus of pyrope, corundum, α -quartz, coesite, stishovite, MgO, brucite, kaolinite, and lizardite
162 using the interatomic potentials in Table 1.

163 A Newton-Raphson optimizer, with Broyden-Fletcher-Goldfarb-Shanno (BFGS)
164 updating of the Hessian matrix, was used for energy minimization. When the gradient norm
165 reached 0.1, we switched to rational function optimization (RFO) to ensure that the final state
166 attained had positive definite curvature. The phonon density of states was also calculated to
167 verify the absence of imaginary modes within the Brillouin zone.

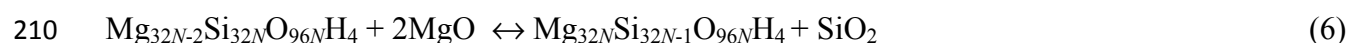
168 Energy minimizations were performed on the majorite structure with both charged and
169 charge-neutral point defects. Intrinsic vacancies were created by removal of a single atom or
170 bound Mg-O pairs where the Mg and O are nearest neighbors. Using the Kröger-Vink defect
171 notation, the intrinsic vacancy defects are expressed as V_{Mg}'' , V_{Si}'''' , and $V_{\text{O}}^{\cdot\cdot}$. We calculated
172 Schottky defect energies in the form of vacancies where the negatively charged cation vacancy is
173 balanced by a positively charged oxygen vacancy. For mass balance, the atoms that are removed
174 are assumed to form a crystalline solid whose lattice energy also contributes to the Schottky
175 defect energy. The extrinsic defects OH_0^{\cdot} , Al_{Si}' , Al_{Mg}' , $[\text{V}_{\text{Mg}} + 2\text{OH}_0]^X$, $[\text{V}_{\text{Si}} + 4\text{OH}_0]^X$, $[\text{Al}_{\text{Si}} +$
176 $\text{Al}_{\text{Mg}} + \text{V}_{\text{Mg}} + 2\text{OH}_0]^X$, and $[\text{Al}_{\text{Si}} + \text{Al}_{\text{Mg}} + \text{V}_{\text{Si}} + 4\text{OH}_0]^X$ were introduced by generating
177 vacancies and introducing impurities as appropriate. For the OH_0^{\cdot} defect, the H atom was
178 initially placed at three different positions relative to each oxygen site and energy minimization
179 calculations were run to determine the lowest energy configuration. The lowest energy
180 configuration was then used for the high- P calculations and we do not see a change in the

181 relaxed hydrogen configuration up to 25 GPa. The difference in energy between the defective
182 and the defect-free majorite lattice was taken to be the defect formation energy. Calculations
183 with a single $[V_{Mg} + 2OH_O]^X$ or $[V_{Si} + 4OH_O]^X$ defect complex per unit cell contain 0.56 – 1.1
184 wt% H₂O and thus additional simulations were performed using 2 x 2 x 2 supercells (1280
185 atoms) for a more realistic concentration of hydrogen within the system (700 – 1400 ppm wt
186 H₂O) and to assess the influence of defect-defect interactions through the periodic boundary
187 conditions. The initial atomic positions of impurities were determined visually using GDIS
188 (Fleming and Rohl 2005) and confirmed after optimization. The lattice parameters for the
189 pressure of interest were generated from constant pressure optimizations of the defect-free, bulk
190 cell. Charged defect calculations are performed in the presence of a uniform neutralizing
191 background charge at constant volume. The initial fractional coordinates for the high-pressure
192 calculations involving charged defects were taken from the optimization at the previous lower
193 pressure. This ensures that a consistent configuration is being considered as a function of
194 pressure. Calculations involving majorite with charge-neutral defect complexes or any
195 calculation involving a defect-free phase were performed at constant pressure.

196 Complementary first-principles simulations were conducted at zero-pressure and $P = 20$
197 GPa for the most energetically favorable charge-balanced defect complexes as determined by the
198 atomistic simulations. Static, DFT calculations were performed with VASP (Kresse and
199 Furthmüller 1996a, 1996b). Ultrasoft pseudopotentials were used and calculations were
200 performed using the Perdew-Wang 1991 (PW91) formalism of the generalized gradient
201 approximation (GGA) for the exchange-correlation functional (Perdew 1991). All first-
202 principles calculations were performed using a plane-wave cutoff of 600 eV with an energy
203 convergence criterion of 0.001 eV for optimization. The majorite calculations are performed at

204 the Γ point for Brillouin zone sampling due to the size of the unit cell. In contrast, the MgO and
205 SiO₂ calculations are averaged over Monkhorst-Pack grids of dimensions 16 x 16 x 16 and 8 x 8
206 x 8 k-points, respectively. To increase computational efficiency, all structures were first relaxed
207 at constant volume then subsequently relaxed at constant pressure.

208 The relative stability of the two defect mechanisms, $[V_{\text{Mg}} + 2\text{OH}_\text{O}]^X$ and $[V_{\text{Si}} + 4\text{OH}_\text{O}]^X$
209 was determined by calculating the enthalpy according to the reactions;



211 and



213 where N is the number of unit cells, with the assumption that the $[V_{\text{Mg}} + 2\text{OH}_\text{O}]^X$ defects are non-
214 interacting. The enthalpy of SiO₂ was calculated while accounting for the α -
215 quartz→coesite→stishovite phase transitions as a function of increasing pressure. The MgO and
216 SiO₂ calculations were performed using the same interatomic potentials (GULP) and
217 pseudopotentials (VASP) as for the majorite calculations, and the initial unrelaxed structures
218 were taken from the American Mineralogist Crystal Structure Database (AMSCD) (Hazen 1976;
219 Levien and Prewitt 1981; Levien et al. 1980; Ross et al. 1990). This reaction does not involve
220 free H₂O due to the difficulty of modeling the energetics of supercritical water.

221 **Results**

222 **Validation of calculations**

223 The calculated majorite structure (Figure 1) (Supplemental data: Table S2) reproduces
224 the experimentally determined structure (Angel et al. 1989) as we find good quantitative
225 agreement between our calculated results and those previously determined from both theory and
226 experiment (Table 2). The structural parameters are within 0.6% of the experimental values,

227 while the errors are less than 6% for most elastic constants with the exception of C_{12} and C_{16}
228 (Table 3). Our calculated zero-pressure bulk modulus and shear modulus are within the spread
229 of experimental results and at $P = 10$ GPa deviate from experimental data (Sinogeikin and Bass
230 2002) by less than 3.5% (Table 3; Supplemental data: Figure S1). Results from our static lattice-
231 energy calculations (SLEC) and the results from Vinograd et al. (2006) were obtained using
232 essentially the same potential models, except for changes to the truncation of the Buckingham
233 potentials and the inclusion of a fourth-order spring constant in the shell model. Hence, the
234 agreement here is to be expected. For phases other than majorite, we find agreement between our
235 calculations and experimentally determined values (Supplemental data: Table S3, Figure S2),
236 with differences of less than ~5% for all structural parameters and ~13% for most bulk moduli.
237 The greatest differences in bulk moduli are for MgO and brucite due to the inability of a simple
238 shell-model to capture the well-known Cauchy violation ($C_{12} \neq C_{14}$) in periclase (Catlow et al.
239 1976) and the limited transferability of the interatomic potentials to non-silicates. Our first-
240 principles calculations reproduce the experimental structure and are consistent with previous
241 DFT-GGA results (Table 2) (Supplemental data: Table S2). The generalized gradient
242 approximation used here tends to lead to a systematic overestimation of structural parameters
243 when compared to experiment, consistent with the observations in the present study. The axial
244 ratio calculated at $P = 20$ GPa using DFT results is only 0.3% smaller than the force field
245 approach.

246 **Defect energies in the absence of water incorporation**

247 The enthalpy of charged Mg, Si, and O, vacancy formation in MgSiO_3 garnet were
248 calculated up to $P = 25$ GPa. The $^{\text{VIII}}\text{Mg}_2$ and $^{\text{IV}}\text{Si}_2$ sites are found to have the lowest energetic
249 cost for forming Mg and Si vacancies (Table 4; Supplemental data: Figure S3). The octahedral

250 site is significantly less favorable for both Mg and Si vacancy defects. The Schottky defect with
251 the lowest energy ($E_{\text{Schottky}} = 4.48 - 7.24$ eV) is the $[V_{\text{Mg}2} + V_{\text{O}5}]^X$ defect (Table 4) in which the
252 Mg-vacancy and O-vacancy are nearest neighbors with an additional energy cost of $0.07 - 0.26$
253 eV when Mg2 and O5 vacancies are not nearest neighbors. Formation of a vacancy at the Mg1
254 site, which is bonded to all 6 oxygens, has a greater Schottky defect energy at zero-pressure
255 when the vacancies at the O1 and O2 sites are not nearest neighbors. Conversely at high
256 pressure, lower Schottky defect energies tend to be associated with Mg and O vacancies that are
257 nearest neighbors with the exception of $V_{\text{Mg}1}$ neighboring $V_{\text{O}1}$ or $V_{\text{O}6}$. When considering the
258 silicon sites, $^{\text{IV}}\text{Si}2$ vacancies have the lowest Schottky defect energies (Table 4).

259 **Protonation mechanism**

260 Protonation of the O1, O4, and O5 sites have energies 0.3 - 0.6 eV lower than O2, O3,
261 and O6 at zero pressure (Figure 2). The protonation energetics can be explained by whether Si
262 (higher energy) or Mg (lower energy) occupies the octahedral site to which the protonated
263 oxygen is bonded. Among the octahedral-Mg oxygen sites, the O5 site is the most favorable site
264 for protonation with a defect formation energy 0.09-0.1 eV lower than O4 and O1. Protonation
265 of the O6 site is 0.20-0.21 eV less favorable compared to the other 2 sites (O2 and O3) involved
266 in Si octahedra.

267 At all pressures, the O5 site is the most likely to bind a hydrogen atom and the O5
268 protonation enthalpy increases with pressure at a smaller rate than for the other oxygen sites
269 (Figure 2). Furthermore, protonation of the oxygen sites involved in Si octahedra become less
270 favorable with pressure relative to the sites involved in Mg octahedra.

271 Based on the energetics associated with creating charged cation and oxygen vacancies,
272 neutral Schottky defects, and protonating the oxygen sites, we propose four distinct charge-

273 balanced hydrogen incorporation mechanisms in majorite. These mechanisms are $[V_{\text{Mg}2} +$
274 $2\text{OH}_{\text{O}5}]^X$, $[V_{\text{Mg}3} + 2\text{OH}_{\text{O}5}]^X$, $[V_{\text{Si}2} + 4\text{OH}_{\text{O}6}]^X$, and $[V_{\text{Si}4} + 2\text{OH}_{\text{O}2} + 2\text{OH}_{\text{O}3}]^X$. The proposed
275 mechanisms include the tetrahedral, octahedral, and dodecahedral sites. The defect structures, as
276 optimized at zero-pressure using the force field approach, are shown in Figure 3. We consider
277 hydrogen incorporation into the dodecahedral site as $[V_{\text{Mg}2} + 2\text{OH}_{\text{O}5}]^X$, into the octahedral sites
278 as either $[V_{\text{Mg}3} + 2\text{OH}_{\text{O}5}]^X$ or $[V_{\text{Si}4} + 2\text{OH}_{\text{O}2} + 2\text{OH}_{\text{O}3}]^X$, and into the tetrahedral site as the
279 hydrogarnet-type defect $[V_{\text{Si}2} + 4\text{OH}_{\text{O}6}]^X$. The optimized hydrogarnet defect consists of the 4 H
280 atoms lying outside of the Si-vacant tetrahedra along the edges and this configuration is
281 confirmed by the DFT calculations. The other three optimized defects show the H atoms
282 pointing inward toward the vacancy and region of negative charge. The DFT calculations also
283 result in the H atoms pointing inward for the $[V_{\text{Mg}3} + 2\text{OH}_{\text{O}5}]^X$ defect. However, there is a
284 difference in direction that the H atoms point. The force field calculations yield a configuration
285 in which the H atoms lie in the plane formed by the O4 and O5 atoms with the H atoms pointing
286 toward opposite O4 atoms ($\angle\text{O}5\text{-H-O}1 = \sim 110^\circ$). The DFT optimization results in the H atoms
287 pointing toward opposite O1 atoms ($\angle\text{O}5\text{-H-O}1 = \sim 160^\circ$).

288 The $[V_{\text{Mg}3} + 2\text{OH}_{\text{O}5}]^X$ octahedral-based defect has formation energy 0.07 eV less than the
289 dodecahedral-based $[V_{\text{Mg}2} + 2\text{OH}_{\text{O}5}]^X$ defect at zero-pressure (Supplemental data: Figure S4).
290 The formation enthalpy difference between the two different Mg defects decreases to 0.01 eV at
291 $P = 25$ GPa. Thus, our interpretation is that H-substitution balanced by Mg vacancies is as likely
292 to occur at octahedral sites as it is to occur at dodecahedral sites. At $P = 0$ GPa, the hydrogarnet
293 defect $[V_{\text{Si}2} + 4\text{OH}_{\text{O}6}]^X$ is 3.56 eV more favorable than hydrogen incorporation into the
294 octahedral site that is normally occupied by silicon (Supplemental data: Figure S4). The
295 enthalpy difference between the Si-based hydrogen defects increases with increasing pressure to

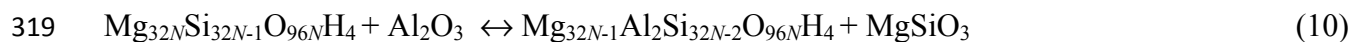
296 3.96 eV at 25 GPa, and therefore the octahedral defect is not expected at any relevant pressure.
297 The enthalpy for reaction 6, which is used to compare the relative stability of the hydrogarnet
298 defect with the $[V_{Mg3} + 2OH_{O5}]^X$ defect, is negative at all pressures (Figure 4) indicating that the
299 hydrogarnet defect should be significantly more stable in majorite at mantle pressures. The
300 stability of the hydrogarnet defect is verified by the DFT calculations (Table 5). The partitioning
301 of hydrogen between the Mg3 sites and Si2 sites can be calculated from the equilibrium constant,
302 K , of reaction 6 as;

$$303 \quad D^{Si2/Mg3} = K = \exp \frac{-\Delta G}{RT} \sim \exp \frac{-\Delta H}{RT} \quad (8)$$

304 Because of a greater number of configurations with the Mg site over the Si site, entropic effects
305 will increase ΔG at high temperatures. Therefore, as an upper bound, the partition coefficient at
306 20 GPa and 1800 K is $D^{Si2/Mg3} \approx 200$.

307 **Effect of Al on OH incorporation**

308 Al is most likely to be incorporated into the majorite structure at either the Si2 tetrahedral
309 or the octahedral sites: the Al_{Si4}' defect has a formation enthalpy that is only 0.13 eV less than
310 that of the Al_{Si2}' defect at zero-pressure and their enthalpies are equal to each other at 25 GPa.
311 The Al_{Mg3}' defect has a formation enthalpy that is at least 1.1 eV less than the enthalpy
312 associated with Al substitution for dodecahedral Mg over the entire pressure range. Therefore,
313 we propose that Al is incorporated into majorite via a coupled substitution with octahedral Mg
314 and either octahedral Si4 or tetrahedral Si2. We calculate the formation enthalpy of the $[V_{Mg3} +$
315 $2OH_{O5}]^X$ defect and the $[V_{Si2} + 4OH_{O6}]^X$ hydrogarnet defect in the presence of a coupled Al-
316 substitution either as $[Al_{Mg3} + Al_{Si2}]^X$ or $[Al_{Mg3} + Al_{Si4}]^X$. Based on the mass-balanced reactions;
317 $Mg_{32N-1}Si_{32N}O_{96N}H_2 + Al_2O_3 \leftrightarrow Mg_{32N-1}Al_2Si_{32N-1}O_{96N}H_2 + MgSiO_3$ (9)
318 and



320 where Al_2O_3 is corundum and MgSiO_3 is majorite, both the $[\text{V}_{\text{Mg}3} + 2\text{OH}_{\text{O}5}]^X$ and the $[\text{V}_{\text{Si}2} +$
321 $4\text{OH}_{\text{O}6}]^X$ are more stable in the presence of a coupled Al-substitution at all pressures (Figure 5).
322 Additionally, according to reaction 7 (Figure 4), the presence of Al serves to further stabilize the
323 hydrogarnet defect relative to the $[\text{V}_{\text{Mg}3} + 2\text{OH}_{\text{O}5}]^X$. The reaction enthalpy as a function of
324 pressure for reactions 6 and 7 goes through a maximum due to the coesite-stishovite phase
325 transition in SiO_2 . The maximum in reaction 6 occurs at 10-15 GPa but in reaction 7 it occurs at
326 7.5-10 GPa. We interpret this as the hydrogarnet defect being more energetically favorable at
327 lower pressures in the presence of Al.

328 **Influence of defect-defect interactions**

329 Comparison of the defect energies associated with both the single unit cell and 2 x 2 x 2
330 supercell of Al-free majorite shows that interaction of periodic images of the hydrogen defects is
331 insignificant ($\Delta H_{\text{def}} \leq 0.03$ eV) (Supplemental data: Figure S4). The defect-defect interactions
332 in aluminous majorite are more significant with the supercell calculations (0.4 wt% Al_2O_3)
333 resulting in hydrous defect formation enthalpies that are up to 0.39 eV greater than the
334 calculations using a single unit-cell (3.2 wt% Al_2O_3).

335 **Wave speeds in hydrous majorite**

336 To examine quantities that could provide geophysical evidence of hydrogen incorporation
337 in garnet in the upper mantle and transition zone, the Voigt-Reuss-Hill averages of the bulk and
338 shear moduli were calculated from the elastic constants (Anderson 1963) derived from the force
339 field calculations (Table 3) along with the compressional and shear acoustic velocities, V_p and V_s .
340 There is a negligible effect of water on both V_p and V_s for majorite with 700 – 1400 ppm wt H_2O
341 at 25 GPa (Figure 6). At these concentrations, body wave speeds are reduced by only ~0.2%,

342 unlikely to be detectable by seismological measurements within the limits of radial seismic
343 profile uncertainties (Matas et al. 2007). When normalized to the same water concentration
344 (1400 ppm wt H₂O) over the pressure range of this study, the shear modulus of majorite with the
345 $[V_{\text{Si}2} + 4\text{OH}_{\text{O}6}]^X$ defect is 0.3% greater than with the $[V_{\text{Mg}3} + 2\text{OH}_{\text{O}5}]^X$ defect. There is even less
346 of a difference between the bulk moduli (<0.2%) and no difference between the densities as a
347 function of defect mechanism. Significant effects on body-wave speeds can only be seen at
348 concentrations of >0.5 wt% water with reductions in V_p and V_s of 1-2% at transition zone
349 pressures. However, such concentrations of water in majoritic garnets are unlikely in Earth's
350 mantle (Beran and Libowitzky 2006)

351 Discussion

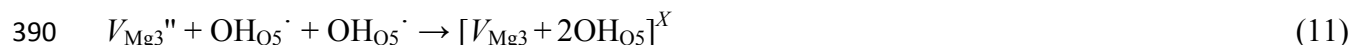
352 Defect Mechanisms

353 Bolfan-Casanova et al. (2000) synthesized tetragonal MgSiO₃ majorite at 17.5 GPa and
354 ~1800 K with ~680 ppm wt H₂O. They argue against the hydrogarnet substitution based on the
355 IR spectra citing the volume expansion of the Si-O tetrahedra (Lager et al. 1989) and energetic
356 feasibility of the hydrogarnet defect formation only at large water contents (Rossman and Aines
357 1991). The OH-absorption band in synthetic majorite (Bolfan-Casanova et al. 2000) is centered
358 80 cm⁻¹ lower and is 65 cm⁻¹ broader compared to the hydrogarnet OH-absorption band in
359 pyrope synthesized at high-pressure (Withers et al. 1998). The volume expansion of the
360 tetrahedra in andradite garnets (Lager et al. 1989) has been used to explain the apparent abrupt
361 dewatering of pyrope at high-pressure (Withers et al. 1998). However, a more recent study
362 (Mookherjee and Karato 2010) shows that pyrope does not dehydrate abruptly at $P = \sim 7$ GPa.
363 Natural grossular garnets with low-OH contents have complex IR spectra and are thus proposed
364 to have substitution of H at the dodecahedral and octahedral site but no evidence for these

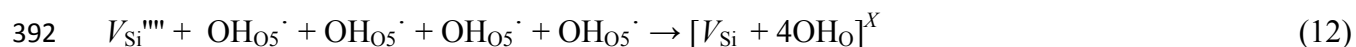
365 substitutions was presented (Rossman and Aines 1991). Our results show that even at low-water
366 contents, the hydrogarnet defect is likely to form in majorite. Synthesis of majorite in the
367 MORB + H₂O system results in a sharp peak centered at 3580 cm⁻¹ (Katayama et al. 2003) which
368 is only 20 cm⁻¹ lower than the hydrogarnet substitution in synthetic pyrope (Ackermann et al.
369 1983). For the hydrogarnet defect in majorite ($P = 0$ GPa), our calculated bond lengths using
370 force field methods, $d(\text{O-O}) = 2.83$ and 3.24 Å for the shared and unshared edges, are shorter
371 than those in grossular ($d(\text{O-O}) = 3.08$ and 3.29 Å) also calculated using interatomic potentials
372 (Wright et al. 1994). Thus, the incorporation of hydrogen through the hydrogarnet defect causes
373 a greater tetrahedral volume expansion in grossular than in majorite due to a greater lengthening
374 of the 2 shared tetrahedral edges. This greater lengthening of the shared edges in grossular is
375 energetically favorable due to Ca, with its larger ionic radius, occupying the dodecahedral sites.
376 Additionally, our DFT optimizations of the hydrogarnet defect result in $d(\text{H...O}) = 2.26$ - 2.34 Å,
377 which is shorter than $d(\text{H...O}) = 2.49$ - 2.62 Å and $d(\text{H...O}) = \sim 2.23$ - 2.54 Å for katoite and
378 hydropyrope calculated in a previous first principles study (Nobes et al. 2000). The shorter
379 $d(\text{H...O})$ in majorite relative to hydropyrope is related to the O-H...O angle. The longer
380 calculated distances in hydropyrope are associated with O-H...O = 113-120° compared to 146-
381 147° in our majorite calculations. Based on shorter O...O and H...O distances, we expect the
382 OH-stretching vibrational frequency to be lower in majorite when compared to other garnets
383 (Libowitzky 1999). Thus it appears that the variation in the vibrational peak positions for the
384 hydrogarnet defect in garnet can be attributed to differences in major and trace element
385 chemistry and possibly the presence of an additional substitution mechanism.

386 Our calculated defect binding energies show that isolated hydroxyl groups are unlikely in
387 the majorite structure and hydrogen is associated with cation vacancies. The defect binding

388 energies for protonation of the $V^{\text{VI}}\text{Mg}$ site and the formation of the hydrogarnet defect are
389 calculated according to the reactions;

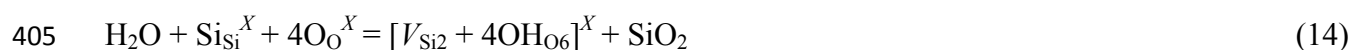
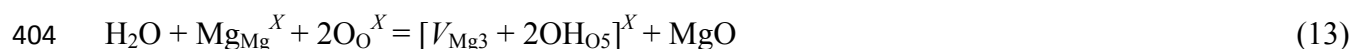


391 and



393 The energetics for formation of the hydrogarnet and $[V_{\text{Mg}^{3+}} + 2\text{OH}_{\text{O}5}]^X$ defects are thus -2.19 eV/H
394 and -1.09 eV/H at zero-pressure. The binding energies become more exothermic with increasing
395 pressure to -2.87 eV/H and -1.64 eV/H at 25 GPa confirming that isolated defects become less
396 favorable at high pressure. The preferential formation of the hydrogarnet defect is consistent
397 with atomistic simulations of hydrogen defect formation in ringwoodite (Blanchard et al. 2005).
398 However, Blanchard et al. (2005) show a significantly greater driving force for hydrogen to be
399 bound to cation vacancies in ringwoodite with defect binding energies of -15.80 eV/H and -10.36
400 eV/H. This is consistent with the greater H₂O storage capacity of ringwoodite (e.g., Bolfan-
401 Casanova 2005).

402 We also compare the relative defect energies of the two defect mechanisms through the
403 reaction of majorite with water as:



406 The reaction energies are thus calculated according to;

$$407 \quad E_{12} = E_{\text{Mg-OH}} + E_{\text{PT}} + U_{\text{MgO}} \quad (15)$$

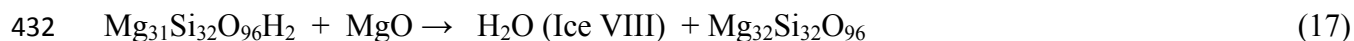
$$408 \quad E_{13} = E_{\text{Hydrogarnet}} + 2E_{\text{PT}} + U_{\text{SiO}_2} \quad (16)$$

409 where E_{PT} is the proton transfer energy and assumed to be -9.74 eV at zero-pressure. The
410 derivation of E_{PT} and the full Born-Haber thermochemical cycle for hydrolysis reactions can be

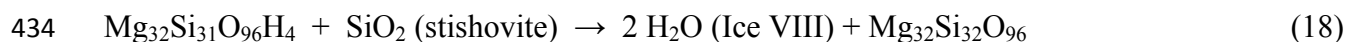
411 found elsewhere (Catlow 1977; Wright et al. 1994). Our zero-pressure calculations show that the
412 hydrogarnet defect is more favorable by 1.44 eV with large negative energies of -6.51 eV/H and
413 -7.95 eV/H for reactions 12 and 13. Thus, it is possible that both types of defects occur in
414 majorite with the hydrogarnet defect likely to be dominant. This is consistent with IR spectra
415 that show a deviation from a strict hydrogarnet substitution (Bolfan-Casanova et al. 2000).
416 Atomistic simulations of defect mechanisms in the olivine polymorphs also show that one defect
417 mechanism tends to be favored over the other. In the case of ringwoodite, both mechanisms are
418 energetically favorable with reaction energies of -3.08 eV/H and -6.49 eV/H (Blanchard et al.
419 2005) and as with majorite, the hydrogarnet is more likely to be dominant. The hydrogarnet
420 defect is also likely to occur in olivine with a reaction energy of 0.4 eV/H compared to 1.5 eV/H
421 for the $[V_{\text{Mg}} + 2\text{OH}_O]^X$ defect (Walker et al. 2006). Conversely, the $[V_{\text{Mg}} + 2\text{OH}_O]^X$ is 5 eV more
422 favorable than the hydrogarnet defect in wadsleyite (Walker et al. 2006).

423 Comparison of our DFT-GGA results at 20 GPa (Table 5) with the work of Panero
424 (2010) confirms that the hydrogarnet defect is more likely to occur in majorite than in
425 ringwoodite. The $[V_{\text{Mg}} + 2\text{OH}_O]^X$ defect is 0.54 eV/H more favorable in ringwoodite than in
426 majorite, while the hydrogarnet defect formation enthalpy in majorite is 0.12 eV/H less than in
427 ringwoodite. Reaction 3 shows that the hydrogarnet defect is more stable in ringwoodite by 0.17
428 eV/H (Panero 2010) compared to 0.82 eV/H in majorite.

429 The stability of the hydrous defects relative to the anhydrous phase in the presence of free
430 H_2O at high-pressure can be accomplished through static calculations using Ice VIII (Panero
431 2006). The following reactions at 20 GPa are considered;



433 and



435 resulting in calculated static reaction enthalpies of -1.88 eV and -0.47 eV respectively.
436 Considering the heat of fusion of H_2O at ambient conditions (0.06 eV) and assuming the Dulong-
437 Petit limit, the relative enthalpy of reaction 17 increases to 0.09 eV at 20 GPa and 2000 K.
438 However, this represents an upper bound because the entropic effects of supercritical water are
439 not considered here. Thus it appears more likely that the hydrogarnet defect will be stable at
440 transition zone conditions and the $[\text{V}_{\text{Mg}} + 2\text{OH}_\text{O}]^X$ defect may not occur at high P - T in the
441 presence of water. This supports the interpretation that it is solely the hydrogarnet defect found
442 in the IR spectra of Katayama et al. (2003).

443 It is possible that there are other H-defect mechanisms in majorite besides those
444 considered here. Zhang and Wright (2010) show that coupled substitutions of Al and H into
445 forsterite favors hydrogen substitution at the Si site by 1-2 eV/H. Our calculations show that the
446 presence of Al stabilizes the hydrogarnet defect by 2.2-2.4 eV (Figure 4). However, Mookherjee
447 and Karato (2010) propose that water is incorporated into pyrope at high water contents through
448 the $[(\text{Al}+\text{H})_{\text{Si}}]^X$ defect.

449 Majoritic garnet found in diamond inclusions originating from transition zone depths
450 have been found to contain ~1 wt% Na_2O coupled with ~15-20 wt% Al_2O_3 (Stachl 2001).
451 However, these garnet inclusions are most likely anhydrous with the weight percent of major and
452 minor element oxides summing to >100%. Zhang and Wright (2012) show that the presence of
453 Al^{3+} and the monovalent Li ion may increase the potential of olivine to incorporate water, with
454 the hydrogarnet defect being particularly favorable. Therefore it may be possible that coupled
455 substitution of Na^+ and Al^{3+} promotes hydrogen uptake in garnet as well.

478 Lateral heterogeneities in seismic wave speeds in the Earth's upper mantle can be caused
479 by both variations in composition and temperature. The $R(\text{H}_2\text{O})$ ratio of $d\ln(V_s)/d(\text{H}_2\text{O})$ and
480 $d\ln(V_p)/d(\text{H}_2\text{O})$ and the $R(T)$ ratio of $d\ln(V_s)/dT$ and $d\ln(V_p)/dT$ are useful to elucidate the
481 underlying cause of mantle heterogeneities (Li et al. 2011). We calculate $R(\text{H}_2\text{O})$ for Al-free
482 majorite as;

$$483 \quad R(\text{H}_2\text{O}) = \frac{\ln V_s(1400 \text{ ppm wt H}_2\text{O}) - \ln V_s(\text{anhydrous})}{\ln V_p(1400 \text{ ppm wt H}_2\text{O}) - \ln V_p(\text{anhydrous})} \quad (19)$$

484 The $R(T)$ value for majorite was calculated at 16 GPa such that;

$$485 \quad R(T) = \frac{\ln V_s(1473 \text{ K}) - \ln V_s(300 \text{ K})}{\ln V_p(1473 \text{ K}) - \ln V_p(300 \text{ K})} \quad (20)$$

486 based on the ultrasonic measurements of Irifune et al. (2008). $R(\text{H}_2\text{O})$ for ringwoodite was taken
487 from Panero (2010) and Li et al. (2011). The Li et al. (2011) seismic ratios for olivine,
488 wadsleyite, and ringwoodite were determined using experimental and calculated densities, bulk
489 and shear moduli (Inoue et al. 1998; Li et al. 2009; Liu et al. 2009; Mao et al. 2008, 2010;
490 Tsuchiya and Tsuchiya 2009; Wang et al. 2003). Even though water at the ~1000 ppm level has
491 only a minor effect on the absolute body wave speeds (Figure 6), our calculated $R(\text{H}_2\text{O})$ values
492 show that the presence of hydrated majorite is observable (Figure 7) within the typical seismic
493 model uncertainty of ± 0.15 (Karato and Karki 2001). The presence of Al has a significant effect
494 on $R(\text{H}_2\text{O})$, with our calculations showing that R decreases by ~0.2-0.4 in the presence of 3 wt%
495 Al_2O_3 with the Al substituted into the octahedral sites. Additionally, seismic wave speeds are
496 dependent upon the density, bulk modulus, and shear modulus thus the pressure dependence of R
497 is particularly sensitive to the pressure derivatives of these parameters. In addition to pressure
498 and temperature, compositional variations, such as variations in Fe content can strongly
499 influence seismic ratios. However, even when considering the presence of Al, $R(\text{H}_2\text{O})$ for
500 majorite appears to be significantly different than the same ratio for ringwoodite at high

501 pressures with a difference of 0.5-1.2 at 20 GPa. At the base of the transition zone, $R(\text{H}_2\text{O})$ for
502 majorite is indistinguishable from $R(T)$ of ringwoodite calculated by Li et al. (2011) using DFT.
503 $R(T)$ for majorite is ~0.5-1.0 greater than our calculated $R(\text{H}_2\text{O})$ for majorite. Our calculated
504 $R(\text{H}_2\text{O})$ for Al-free majorite is indistinguishable from that of olivine and wadsleyite up to 15 and
505 20 GPa but becomes significantly different in the presence of aluminum. Therefore, it appears
506 that the effect of hydrated, aluminous majorite should be visible in the upper mantle and
507 neglecting it may result in an overestimate of temperature anomalies.

508

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520

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- 760

761 **Figure Captions**

762 **Figure 1.** Crystal structure of defect-free MgSiO₃ tetragonal garnet optimized using
763 force fields. The two octahedral sites are occupied by Si (pink) and Mg (blue). Mg atoms (light
764 blue) occupy two unique interstitial sites. Three unique tetrahedral sites are occupied by Si (red).

765 **Figure 2.** Enthalpy associated with protonating each oxygen site calculated using the
766 force field approach.

767 **Figure 3.** OH-defect structures in MgSiO₃ majorite optimized using force fields.
768 Hydrogen atoms are light blue and the oxygen atoms are color-coded according to atomic site
769 where O1=red, O2=light green, O3=dark blue, O4=yellow, O5=dark green, O6=purple. (a)
770 [$V_{Mg2} + 2OH_{O5}$]^X (b) [$V_{Mg3} + 2OH_{O5}$]^X (c) [$V_{Si4} + 2OH_{O2} + 2OH_{O3}$]^X (d) “Hydrogarnet”-type [V_{Si2}
771 + 4OH_{O6}]^X.

772 **Figure 4.** Enthalpies of reactions 6 (Al-free) and 7 (Al₂O₃ = 0.4 wt%) calculated as a
773 function of pressure using the force field approach. Negative values of the enthalpy correspond
774 to the hydrogarnet defect being favored.

775 **Figure 5.** Calculated enthalpies (reactions 8 and 9) using force fields for hydrogen
776 incorporation via (a) Mg and (b) Si vacancies in the presence of a coupled-substitution of Al for
777 ^{IV}Si or ^{VI}Si and ^{VI}Mg as a function of pressure. Open symbols represent calculations using a 2 x
778 2 x 2 supercell, and the filled symbols represent calculations using the conventional tetragonal
779 unit cell.

780 **Figure 6.** (a) V_p and (b) V_s for Al-free anhydrous and hydrous majorite calculated as a
781 function of pressure using force fields.

782 **Figure 7.** The force field calculated majorite $d\ln V_s/d\ln V_p$ due to compositional changes
783 resulting from OH incorporation compared to experimental and computational results for the

784 olivine polymorphs (Li et al., 2011). The results from this study are shown by red squares ($[V_{Mg3}$
785 $+ 2OH_{O5}]^X$, $C_{water} = 1400$ ppm), blue triangles ($[V_{Si2} + 4OH_{O6}]^X$, $C_{water} = 1400$ ppm), light blue,
786 open squares ($[V_{Si2} + 4OH_{O6}]^X$, $C_{water} = 1.13$ wt%) and light blue triangles ($[V_{Si2} + 4OH_{O6}]^X$, C_{water}
787 $= 1.13$ wt%, $C_{Al2O3} = 3.2$ wt%). Experimental results (filled black symbols) for forsterite
788 (square) (Mao et al. 2010), wadsleyite (triangle) (Mao et al. 2008), and ringwoodite (circle)
789 (Inoue et al. 1998; Wang et al. 2003) are shown. Additional computational results (black open
790 symbols and dashed lines) are also shown for forsterite (triangles) (Tsuchiya and Tsuchiya
791 2009), wadsleyite (circles) (Liu et al. 2009), and ringwoodite (squares and dashed line without
792 symbols) (Panero 2010; Li et al. 2009), respectively. For comparison, the thermal $d\ln V_s/d\ln V_p$
793 for ringwoodite (Li et al. 2011) is shown by the orange dotted line.
794

795

Tables

796 **Table 1.** Interatomic potential parameters and ionic charges.

<i>Species</i>	<i>q</i> (e)
Mg(core)	1.7
Si(core)	3.4
Al(core)	2.55
O(core)	0.746527
O(shell)	-2.446527
O _H (core) ^a	-1.2
H(core)	0.35

<i>Interaction</i>			
<i>Buckingham</i>	<i>A</i> (eV)	<i>ρ</i> (Å)	<i>C</i> (eV · Å ⁶)
Mg(core) – O (shell)	1432.8544	0.277265	0.0
Si(core) – O (shell)	1073.4668	0.298398	0.0
Al(core) – O (shell)	1262.2081	0.28637	0.0
Mg(core) – O _H (core)	1015.8587	0.277265	0.0
Si(core) – O _H (core)	761.06168	0.298398	0.0
Al(core) – O _H (core)	894.87465	0.28637	0.0
O(shell) – O(shell)	598.8996	0.314947	26.89746
O(shell) – O _H (core)	598.8996	0.314947	26.89746
O _H (core) – O _H (core)	598.8996	0.314947	26.89746
H(core) – O(shell)	191.6667	0.25	0.0
H(core) – O _H (core)	191.6667	0.25	0.0

<i>Morse</i>	<i>D_e</i> (eV)	<i>a</i> (Å ⁻¹)	<i>r₀</i> (Å)
H(core) – O _H (core)	7.0525	2.1986	0.94285

<i>Spring</i>	<i>k₂</i> (eV/Å ²)	<i>k₄</i> (eV/Å ⁴)
O(core) – O(shell)	56.5598	10000.0

<i>Three-body</i>	<i>k_θ</i> (eV/rad ²)	<i>θ</i> (degrees)
O – ^{IV} Si – O	0.77664	109.47
O – ^{VI} Si – O	2.2955	90.0
O – ^{IV} Al – O	1.2883	109.47
O – ^{VI} Al – O	1.8807	90.0

797

798 **Table 2.** Calculated structural parameters for tetragonal MgSiO₃ majorite compared to
 799 published experimental and computational data.

<i>Cell parameters</i>	<i>XRD</i> ^a	<i>SLEC</i> This Study	% difference	<i>SLEC</i> ^b	<i>DFT-GGA</i> This Study	<i>DFT-GGA</i> ^b
<i>P</i> = 0 GPa						
<i>a</i> (Å)	11.501(1)	11.506	0.04	11.494	11.638	11.670
<i>c</i> (Å)	11.480(2)	11.416	-0.56	11.392	11.528	11.561
<i>c/a</i>	0.9982(2)	0.9922	-0.60	0.9912	0.9905	0.9907
<i>V</i> (Å ³)	1518.6(4)	1511.27	-0.48	1505.04	1561.34	1574.47
<i>P</i> = 10 GPa						
<i>a</i> (Å)	11.315	11.307	-0.07	–	–	–
<i>c</i> (Å)	11.214	11.211	-0.03	–	–	–
<i>c/a</i>	0.9911	0.9915	0.04	–	–	–
<i>V</i> (Å ³)	1435.7	1433.33	-0.17	–	–	–
<i>P</i> = 20 GPa						
<i>a</i> (Å)	–	11.144	–	–	11.251	–
<i>c</i> (Å)	–	11.048	–	–	11.115	–
<i>c/a</i>	–	0.9913	–	–	0.9879	–
<i>V</i> (Å ³)	–	1372.05	–	–	1407.06	–

^aAmbient condition (Angel et al. 1989) and *P* = 9.72 GPa experiments (Yagi et al. 1992) and ; ^bCASTEP (Vinograd et al. 2006)

800

801 **Table 3.** Elastic constants, bulk (K_s) and shear (μ) moduli of tetragonal majorite garnet
 802 (MgSiO_3).

<i>Elastic constants</i>	<i>Experimental</i> (GPa)	<i>SLEC This study</i> (GPa)	<i>SLEC^b</i> (GPa)
<i>P = 0 GPa</i>			
C_{11}	^a 286.4(13)	296.52	295.10
C_{33}	^a 280.1(18)	296.14	–
C_{44}	^a 85.0(7)	86.05	85.23
C_{66}	^a 93.2(11)	94.14	93.66
C_{12}	^a 83.0(29)	112.5	112.7
C_{23}	^a 104.9(24)	102.42	–
C_{16}	^a 1.4(13)	14.30	14.72
<i>P = 10 GPa</i>			
C_{11}	–	347.04	–
C_{33}	–	350.51	–
C_{44}	–	92.99	–
C_{66}	–	103.66	–
C_{12}	–	141.27	–
C_{23}	–	132.47	–
C_{16}	–	21.55	–
<i>P = 20 GPa</i>			
C_{11}	–	392.16	–
C_{33}	–	398.69	–
C_{44}	–	97.96	–
C_{66}	–	109.86	–
C_{12}	–	170.97	–
C_{23}	–	164.06	–
C_{16}	–	26.36	–
<i>Isotropic properties</i>			
<i>P = 0 GPa</i>			
K_s	^a 159.8(44), ^c 167.3(33) ^d 164.4(5), ^e 170(5), ^f 166(3) ^g 166(5), ^h 164(4)	169.3	170.14
μ	^a 89.7(6), ^c 88.3(18), ^d 94.9(2) ^e 89(1), ^f 85(2), ^g 88(2), ^h 87(2)	90.8	–
<i>P = 10 GPa</i>			
K_s	^b 210(4)	206.3	–
μ	^b 103(2)	99.4	–
<i>P = 20 GPa</i>			
K_s	–	242.4	–
μ	–	105.3	–

803 ^aAmbient condition experiments, Mj_{100} (Pacalo and Weidner 1997); ^bVinograd et al. (2006); ^c Mj_{100} (Gwamnesia et
 804 al. 1998); ^dpyrolite minus olivine composition (Irifune et al. 2008); ^e $\text{Mj}_{50}\text{Py}_{50}$ (Liu et al. 2000); ^f Mj_{100} (Sinogeikin
 805 and Bass 2002); ^g Mj_{100} (Sinogeikin et al. 1997a); ^hnatural Catherwood meteorite sample (Sinogeikin et al. 1997b)

806 **Table 4.** Calculated vacancy formation energy and crystalline lattice energies from force fields
 807 implemented in GULP.

<i>Defect</i>	<i>Formation Enthalpy (eV)</i>	
	0 GPa	25 GPa
<i>Unbound vacancies</i>		
$V_{Mg1}^{\cdot\cdot}$	18.89	19.50
$V_{Mg2}^{\cdot\cdot}$	18.77	19.38
$V_{Mg3}^{\cdot\cdot}$	19.43	20.26
$V_{Si1}^{\cdot\cdot}$	76.61	78.89
$V_{Si2}^{\cdot\cdot}$	70.07	71.95
$V_{Si3}^{\cdot\cdot}$	73.39	75.84
$V_{Si4}^{\cdot\cdot}$	72.56	74.36
V_{O1}^{\cdot}	17.06	16.78
V_{O2}^{\cdot}	16.69	16.92
V_{O3}^{\cdot}	15.93	15.56
V_{O4}^{\cdot}	15.96	15.54
V_{O5}^{\cdot}	15.95	15.56
V_{O6}^{\cdot}	17.08	17.31
<i>Bound vacancies</i>		
$[V_{Mg1} + V_{O1}]^x$	35.86	36.34
$[V_{Mg1} + V_{O2}]^x$	35.44	36.32
$[V_{Mg1} + V_{O3}]^x$	34.97	34.99
$[V_{Mg1} + V_{O4}]^x$	35.87	35.03
$[V_{Mg1} + V_{O5}]^x$	34.90	35.01
$[V_{Mg1} + V_{O6}]^x$	36.15	37.07
$[V_{Mg2} + V_{O1}]^x$	35.20	35.24
$[V_{Mg2} + V_{O2}]^x$	35.04	35.24
$[V_{Mg2} + V_{O5}]^x$	34.66	34.68
$[V_{Mg2} + V_{O6}]^x$	35.47	36.59
$[V_{Mg3} + V_{O1}]^x$	35.69	35.88
$[V_{Mg3} + V_{O4}]^x$	36.40	34.81
$[V_{Mg3} + V_{O5}]^x$	34.67	35.04
<i>Phase</i>		
MgO	-30.18	-27.44
α -Quartz	-95.35	-
Stishovite	-	-91.06

808

809 **Table 5.** Enthalpies calculated from first principles at the DFT-GGA level of theory.

	0 GPa	20 GPa
<i>Enthalpy (eV)</i>		
MgO ^a	-12.01	-9.71
SiO ₂ , α -quartz ^a	-23.98	–
SiO ₂ , stishovite ^a	–	-20.55
Majorite ^b	-1147.67	-963.27
<i>Defect Formation Enthalpy (eV/H)</i>		
$V_{\text{Mg}^{3+}} + 2(\text{OH}_{\text{O}5})$	-0.51	-0.62
$V_{\text{Si}^{4+}} + 4(\text{OH}_{\text{O}6})$	-1.37	-1.16
<i>Reaction enthalpy (eV/H)</i>		
Reaction 6	-0.85	-0.82

810 ^a1 formula unit; ^bFull unit cell (8 formula units)

Figure 1.

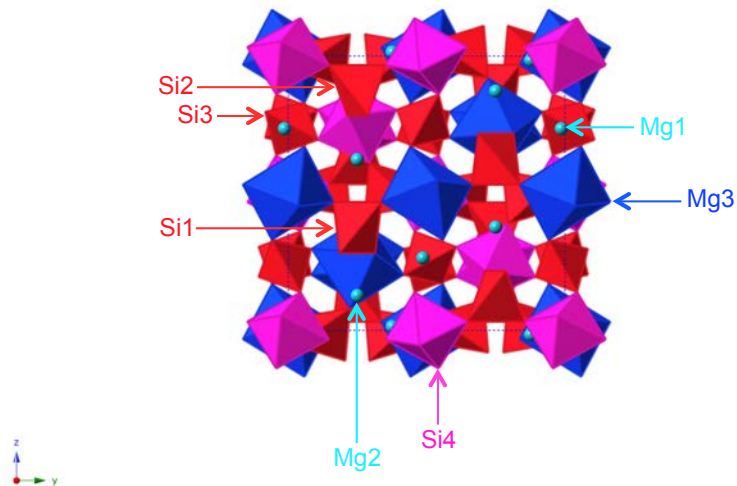


Figure 2.

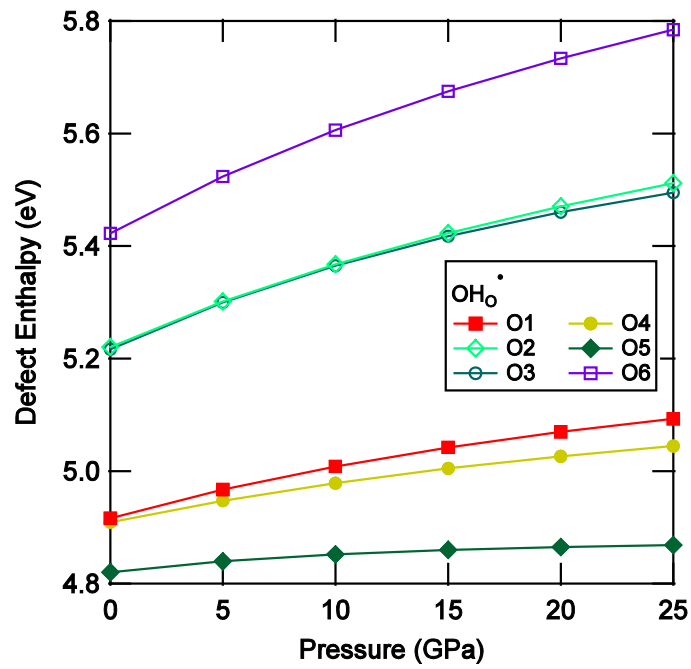


Figure 3.

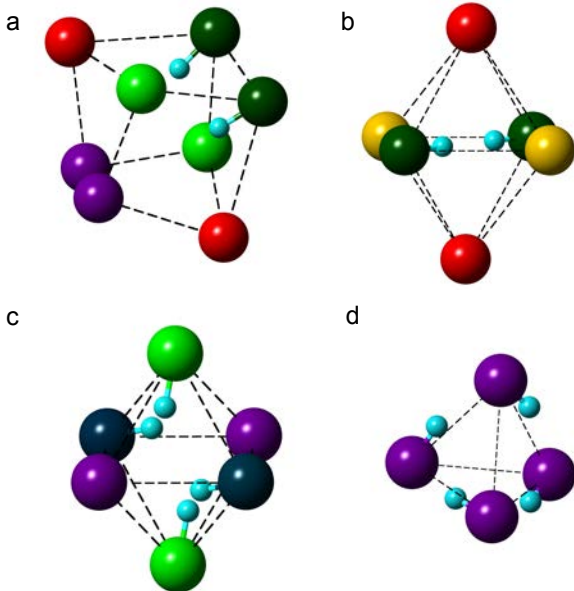


Figure 4.

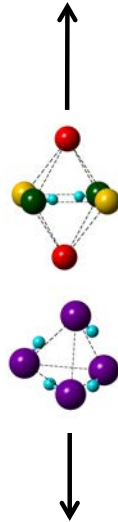


Figure 5a.

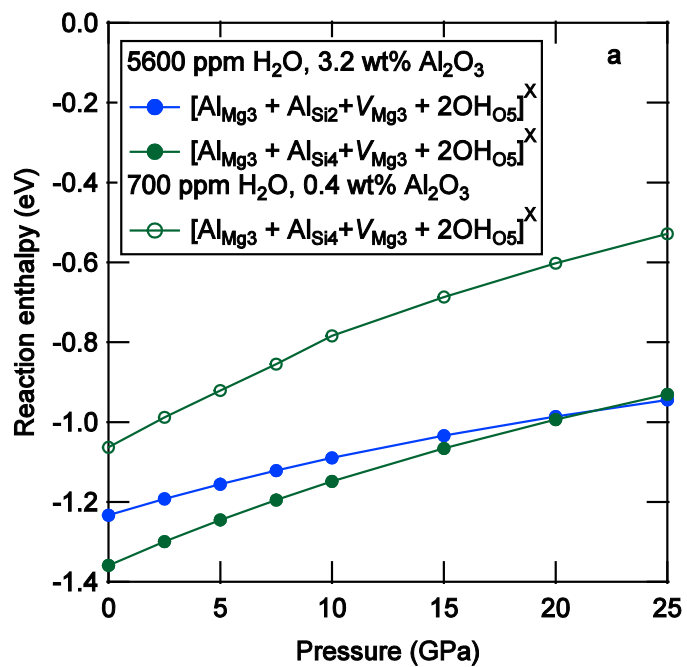


Figure 5b

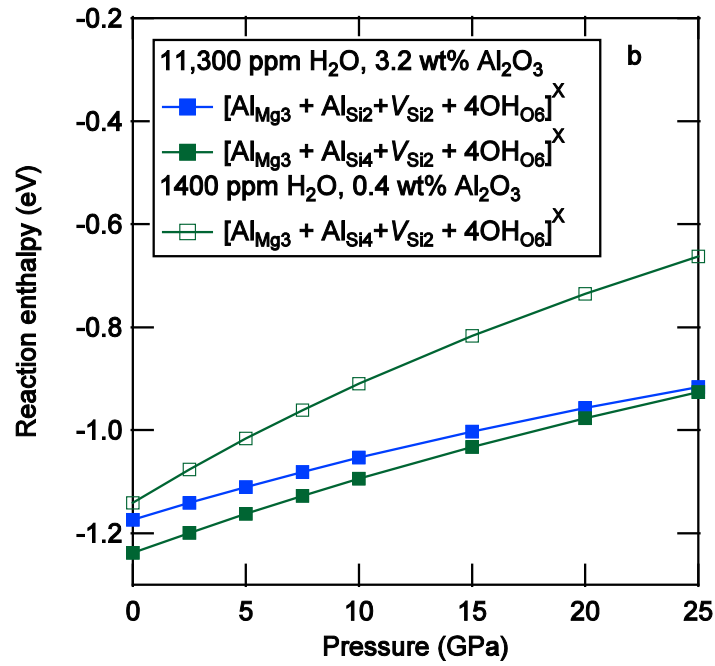


Figure 6a.

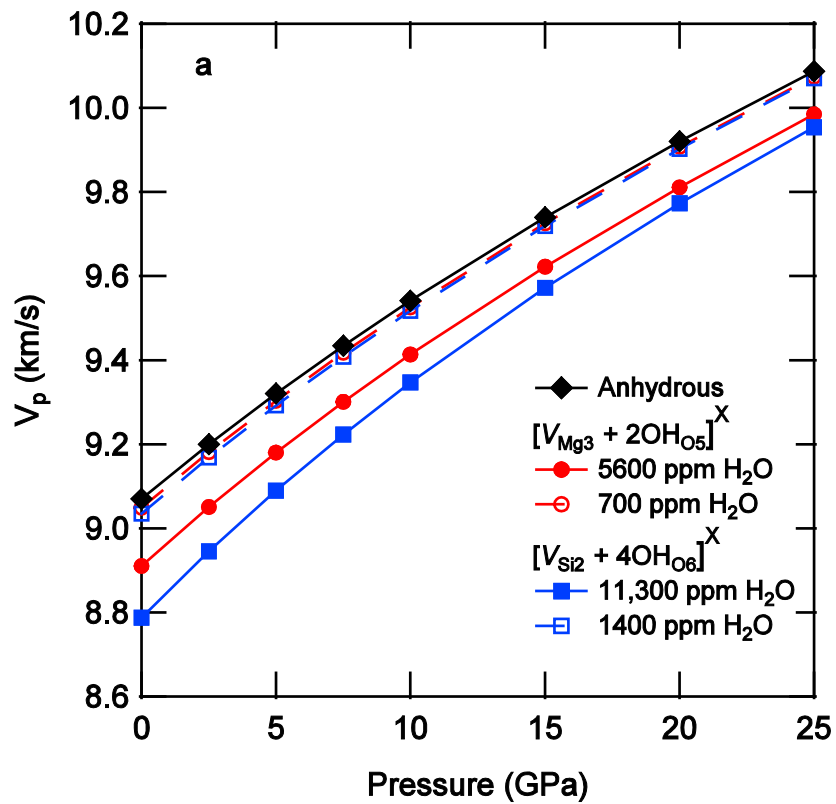


Figure 6b.

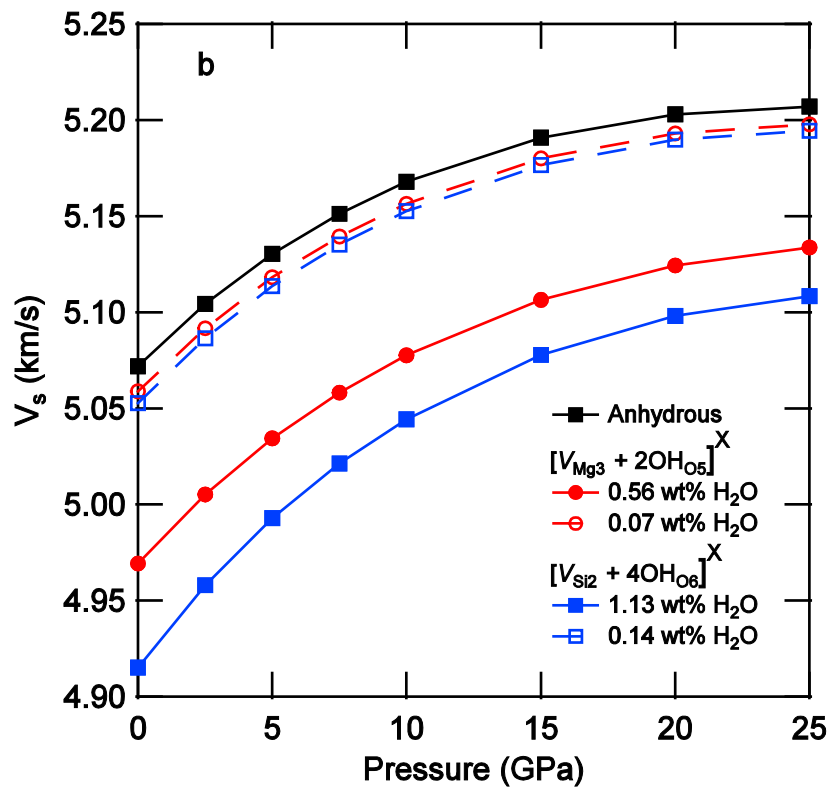


Figure 7.

