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10 **This manuscript “The distribution of hydrogen/water in Al and Ti-containing forsterite:**
11 **A thermodynamic model” is a preprint manuscript uploaded to EarthArxiv which has**
12 **not yet undergone peer review. It has been submitted for review. Subsequent versions**
13 **may have different content.**

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15 **The distribution of hydrogen/water in Al and Ti-containing forsterite: A thermodynamic**
16 **model**

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25 Words:6637

26 Key Words: Forsterite; Water; Hydrogen; DFT; Point Defects; Titanium; Aluminium

27 **Abstract**

28 In forsterite the functional form of water is regard to be hydrogen. The distribution of this
29 hydrogen across different sites in forsterite is important because it determines what rheological
30 properties of forsterite are affected by water and how they are affected. In this study we use
31 lattice dynamic Density Functional Theory (DFT) to build a thermodynamic model of
32 hydrogen in forsterite that contains both Al and Ti sites. We find that Al does not cause
33 significant variation in the distribution of water in forsterite but that Ti does. At low pressures
34 we find that water favours either $(2H)_{Mg}^X$ or $\{Ti_{Mg}^{..}(2H)_{Si}^{..}\}$ with the latter favoured by low
35 temperatures and high Ti contents. As pressure increases $(4H)_{Si}^X$ becomes the dominant site
36 of water even in the presence of enstatite, high temperatures and high Ti contents. Thus two
37 charge balance regimes are seen across normal experimental and upper mantle conditions. We
38 predict the distribution of hydrous products along an upper mantle geotherm. The
39 concentration of $(2H)_{Mg}^X$ likely controls Mg diffusion and conductivity and we find that this

40 peaks at ~100 km depth for 10 wt. ppm water, ~50 km for 100 wt. ppm water and at 0 km for
41 100 wt. ppm water before declining rapidly with depth beyond these points. The concentration
42 of $(4H)_{Si}^X$ likely controls Si diffusion and the strength of forsterite. In relatively dry forsterite
43 we find that there is initially a big increase in the concentration of $(4H)_{Si}^X$ with depth before a
44 certain depth where the concentration of $(4H)_{Si}^X$ becomes insensitive to depth as it is the
45 dominant product. As the crystal gets wetter the initial increase in concentration gets smaller
46 and the depth at which $(4H)_{Si}^X$ becomes the dominant product becomes shallower. For 10 wt.
47 ppm water $(4H)_{Si}^X$ concentration increases by 2 orders of magnitude over the first 200 km of a
48 geotherm before obtaining a near consistent value whereas for 1000 wt. ppm water $(4H)_{Si}^X$ has
49 a consistent concentration throughout the upper mantle. This suggests that nearly dry olivine
50 gets considerably weaker as it descends into the mantle before a certain depth where it has
51 consistent strength whereas wet olivine has a consistent strength throughout the upper mantle.
52 We predict the water exponents of defect concentrations and find that they can vary strongly
53 under different conditions particularly as charge balance regimes change. Water in forsterite
54 thus behaves very differently in different P, T and water concentration regimes and
55 extrapolation of mechanical properties between these regimes is extremely difficult.

56

57 Keywords: Forsterite; Hydrogen; Water; Titanium, Aluminium, DFT

58

59 **1 Introduction**

60 Water is a strong control on the properties of forsterite and olivine. Small amounts of water
61 can lead to significant changes in strength (“hydrolytic weakening”) (Demouchy et al., 2012,
62 Girard et al., 2013a, Fei et al., 2013, Karato and Jung, 2003, Mei and Kohlstedt, 2000a, Mei
63 and Kohlstedt, 2000b, Karato et al., 1986, Mackwell et al., 1985), texture development (Jung
64 and Karato, 2001, Karato et al., 2008) and diffusion of cations and conductivity (Fei et al.,

65 2013, Fei et al., 2018). The upper mantle contains around 20-500 ppm water on average
66 though it is likely most of it is quite dry <50 ppm with some regions considerably more enriched
67 (Hirschmann, 2006, Demouchy and Bolfan-Casanova, 2016). Therefore we must understand
68 the effect of water on olivine to understand the rheological properties of olivine in the upper
69 mantle.

70

71 To determine the effect of water on mechanical properties we must know where it is located.
72 Water that exists on Mg vacancies will have different effects on the properties of olivine than
73 water that exists on Si vacancies for example. Water in forsterite is generally regarded as a
74 series of hydrogen containing defects (see Equation 1) and thus the water sites in forsterite are
75 all sites containing hydrogen and the distribution of water shall also be the distribution of
76 hydrogen.

77 Experimentally there is a long literature examining the question of hydrous defects in olivine
78 (Matveev et al., 2001, Le Losq et al., 2019, Berry et al., 2005, Tollan et al., 2018, Lemaire et
79 al., 2004, Mosenfelder et al., 2006, Mosenfelder et al., 2011, Padron-Navarta et al., 2014, Berry
80 et al., 2007a, Tollan et al., 2017, Blanchard et al., 2017) but in general 4 types of hydrated
81 defects have been observed. These are (using Kroger-Vink notation): $(2H)_{Mg}^x$, $(4H)_{Si}^x$,
82 $\{Ti_{Mg}^{ii}(2H)_{Si}^{''}\}$ and $\{triv_{Mg}(1H)_{Mg}'\}$ where triv is a trivalent atom such as Fe(III) or Al (III) or
83 Cr(III) (Tollan et al., 2017) most commonly Fe(III) (Blanchard et al., 2017). There is
84 considerable disagreement about the relative favourability of these defects under different
85 conditions. $(4H)_{Si}^x$ appears to be favoured at high pressures (Smyth et al., 2006, Xue et al.,
86 2017, Withers and Hirschmann, 2008, Mosenfelder et al., 2006) but this may not be the case in
87 the presence of Ti which forms (at low pressures) $\{Ti_{Mg}^{ii}(2H)_{Si}^{''}\}$ with a water exponent of 1
88 (Tollan et al., 2017) or high temperatures which favour $(2H)_{Mg}^x$ (Walker et al., 2007). It is
89 also important to know not just the most favoured defects but the concentrations of all hydrous

90 defects to precise levels as properties like diffusion can be affected by defects that are present
91 even at ppt levels due to the low concentration of intrinsic defects (Muir et al., 2020).
92 Some theoretical work has been performed on the structure of hydrous defects in olivine. Early
93 studies investigated the effect of hydrogen on defects using interatomic potentials (Wright and
94 Catlow, 1994) but given how point defects alter the electronic structure of the crystal it has
95 proven necessary to use electronic structure methods (Brodholt and Refson, 2000, Haiber et al.,
96 1997, Braithwaite et al., 2002). More recent studies have investigated the interaction between
97 hydrogen and trace elements such as titanium (Berry et al., 2007b, Walker et al., 2007) or boron
98 (Ingrin et al., 2014) or attempted to link atomic scale models of the structure of various hydrous
99 defects with the results of infra spectroscopy (Balan et al., 2011, Umemoto et al., 2011,
100 Braithwaite et al., 2003). In general these studies have confirmed the structure of the various
101 hydrous defects by determining the low energy forms but have not considered the effect of
102 temperature or built a model of their energetic relationships to each other and to intrinsic
103 defects with the exception of $(2H)_{Mg}^X$ and $(4H)_{Si}^X$ (Walker et al., 2007, Qin et al., 2018).
104 Thus in this work we shall use *ab-initio* calculations to build a thermodynamic model and probe
105 the distribution of hydrogen in forsterite. We shall include Ti so as to examine the important
106 $\{Ti_{Mg}^{2+}(2H)_{Si}^{2-}\}$ defect and Al to probe the effect of trivalent elements. These are two elements
107 that occur in olivine to high concentrations (up to around 300 ppm) (De Hoog et al., 2010).

108

109 **2 Methods**

110 *2.1 General Method*

111 In this work we calculated the energy of different isolated defects in forsterite. This was done
112 use lattice dynamics DFT. These energies are then used to calculate the energy of a series of
113 reactions (see Results). We then determine the energy of different concentrations of these
114 defects using the energies of these reactions and configurational entropy calculations and

115 determine the defect concentrations that give the minimum free energy at any particular
116 condition and this is the equilibrium distribution of defects.

117

118 *2.1 Defect calculations using density functional theory*

119 All calculations were performed with planewave DFT using version 16.11 of the CASTEP
120 code (Clark et al., 2005). On-the-fly ultra soft pseudopotentials were used with 2s, 3p and 3s,
121 2s and 2p, 3s and 3p, 1s and 3p, 3s, 4s and 3d electrons in the valence for Mg, O, Si, H and Ti
122 respectively. The PBE (Perdew et al., 1996) exchange correlation functional (a revised GGA
123 functional) was used alongside a planewave cutoff of 1000 eV and a (4x4x4) k-point grid in
124 reciprocal space (Monkhorst and Pack, 1976).

125 A (2x1x2) supercell of forsterite was used into which hydrous vacancies were inserted. After
126 placing defects in the supercell, the structure was then relaxed until the forces on all atoms
127 were less than 0.01 eV/Å and an energy tolerance of 1×10^{-5} eV/atom was repeated. Repeating
128 calculations with increased cutoffs changed the energy of the supercell by <0.1 meV/atom. A
129 (2x1x2) forsterite supercell was used to ensure that there was roughly 10 Å between repeating
130 vacancies in all directions, a distance we found to be sufficient to contain the important atomic
131 relaxations. For simulating $\{2Al_{Mg}^{\bullet}V_{Mg}''\}$ trios a (4x2x4) supercell was used due to the large
132 size of the defect. To approximate the dilute limit volumes were fixed to those of the pure
133 forsterite supercell for both static and QHA calculations. Defect energies were calculated at 0,
134 5, 10 and 15 GPa and at temperatures 1000, 1300, 1500, 1600 and 2000 K.

135 To calculate high temperature free energies the phonons of the most stable arrangements of
136 each type of defect were calculated using finite differences (displacements of 0.01 bohr) in the
137 CASTEP code (Clark et al., 2005). This was performed for at least 5 different volumes for
138 each system and the energy calculated as a function of volume with equations given in Muir et
139 al. (Submitted). The thermal expansion of forsterite was calculated and then at each

140 temperature and pressure the energy of each defect was calculated at the appropriate volume
141 of forsterite at those conditions. More discussion on the approximations involved here is given
142 in the supplementary information.

143 Our method for calculating non-hydrous vacancies is covered in Muir et al. (Submitted). 5
144 different hydrous defects were examined- $(2H)_{Mg}^X$, $(4H)_{Si}^X$, $(1H)'_{Mg}$, H_{Int}^\bullet and $Ti_{Mg}^{\bullet\bullet}(2H)''_{Si}$.
145 In each case their energy was sampled at each possible site in the crystal. $(2H)_{Mg}^X$ and $(1H)'_{Mg}$
146 were be placed at M1 and M2 sites in the crystal replacing a Mg atom. For $Ti_{Mg}^{\bullet\bullet}(2H)''_{Si}$ the
147 Titanium was placed at an M1 or an M2 site replacing a Mg and the $(2H)''_{Si}$ was placed at an
148 adjacent silicon site. The enthalpy of all possible arrangements of these two groups at adjacent
149 sites was calculated (Table S3). For charged defects a correction was applied as outlined in
150 Muir et al. (Submitted).

151 For $(2H)_{Mg}^X$, $(4H)_{Si}^X$, $Ti_{Mg}^{\bullet\bullet}(2H)''_{Si}$ and $(1H)'_{Mg}$ there are multiple possible arrangements of
152 hydrogen in the vacancy. If we consider an arrangement of hydrogen as being each hydrogen
153 bound to a specific oxygen (in an $(OH)^-$ group) we tested every possible arrangement of
154 hydrogen with hydrogens pointing both into and out of the vacancy (Table S1-5). In each case
155 the arrangement with the most stable enthalpy was used at high temperature.

156 2.2 Thermodynamic Minimisation

157 For any pressure and temperature, we first determined the energy of each defect at those
158 conditions. This was done by projecting first along pressure and then along temperature using
159 polynomials and points at 5, 10 and 15 GPa (uncorrected) and 1000, 1500 and 2000 K. The
160 energy of each defect was then placed into the reactions found in the text and the energy of
161 each reaction (E_i) determined at those conditions. We then used a series of minimisations to
162 find the distribution of defects that gave the lowest free energy. In all cases the water content,
163 Ti content and Al content were fixed for each minimisation.

164 Each combination of defects can be represented via a series of variables ($x_1 \dots x_{22}$) where each
165 variable represents one reaction in the text and goes from 0 (reaction does not proceed, all
166 reactants) to 1 (all products).

167 The free energy of each distribution was determined with Equation 1:

$$168 \Delta G = \sum_i \Delta E_i \times x_i - TS_{confa} \text{ Equation 1}$$

169 with the first part related to forming the defects and the second part related to their
170 configurational entropy. The first part is determined by simply the energy (E_i) of each reaction
171 times by how far it progresses (x_i) while the second part is more complex. In short we
172 determine for each defect the different enthalpies of its possible hydrogen arrangements, its
173 placement on different lattice sites and its geometrical arrangements for defects that are
174 pairs/trios and then we use the Gibbs entropy formula with the Stirling approximation to
175 determine the configurational entropy of the whole system. Full details of our configurational
176 entropy calculations and the approximations involved are given in the supplementary
177 information. Using a bespoke solver (information in supplementary information) we vary each
178 variable $x_1 \dots x_{22}$, solving Equation 1 at each point, and do this until the energy no longer
179 decreases and that is determined as the thermodynamic equilibrium distribution.

180 *2.5 Pressure Correction*

181 While DFT generally reliably reproduces pressure derivatives, the absolute pressures
182 calculated by DFT are known to be systematically incorrect in that they are shifted in one
183 direction. To correct for these we used a simple linear correction

$$184 P(V, T) = P^{DFT}(V, T) - P^{DFT}(V_0^{exp}) \text{ Equation 2}$$

185 Where the subscript 0 represents the value of a parameter at a reference volume. For this
186 equation we used V_0^{exp} values of 287.4 \AA^3 for olivine (Isaak et al., 1989), 74.71 \AA^3 for MgO
187 (Speziale et al., 2001) and 832.918 \AA^3 for enstatite (Kung et al., 2004). This provided

188 corrections of -4.95, -4.45 and -3.91 GPa respectively. The energy of our reactions were then
 189 adjusted to account for these different pressure corrections using our calculated dE/dP values.
 190 All pressures are presented corrected unless stated.

191 2.6 Units

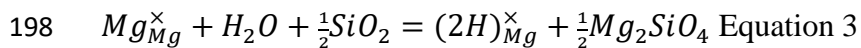
192 In this work water concentrations are always given in wt. ppm H₂O, Ti concentrations in wt.
 193 ppm TiO₂ and Al in wt. ppm Al₂O₃.

194

195 3. Results

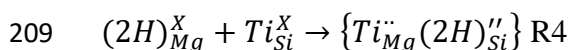
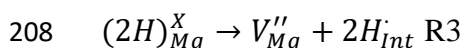
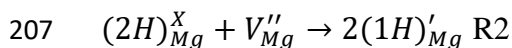
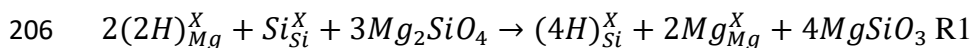
196 3.1 Water Reactions

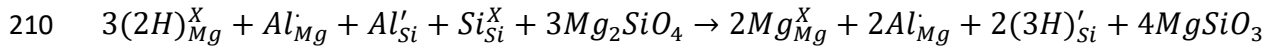
197 Water could adsorb in forsterite via a reaction like:



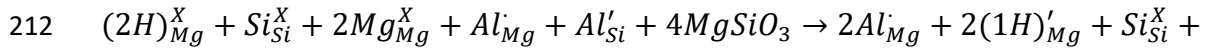
199 Determining the parameters of this reaction is difficult due to the presence of free water.
 200 Instead we can determine the favoured site for water in forsterite by calculating the energy
 201 differences between different sites. This was done for water defects, intrinsic defects and some
 202 selected non-hydrous extrinsic defects. A buffer reaction was used whose progress was set
 203 manually to control the SiO₂ activity. The following reactions were present in our model (using
 204 Kroger-Vink notation):

205 Hydrous Reactions

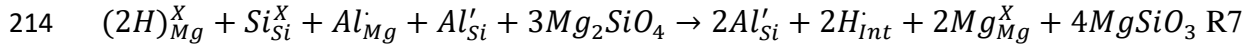




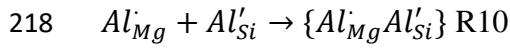
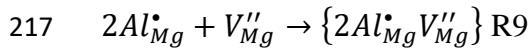
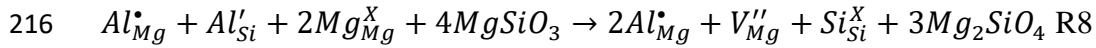
211 R5



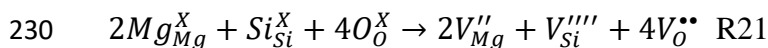
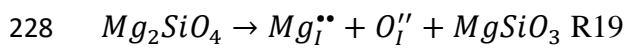
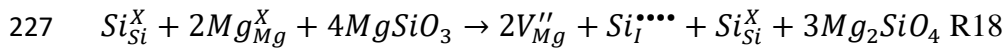
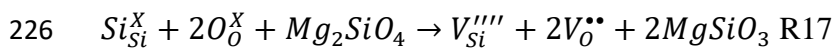
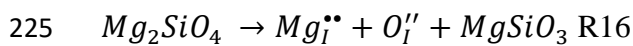
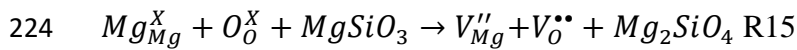
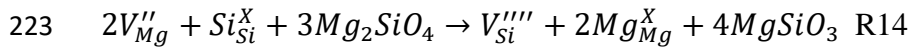
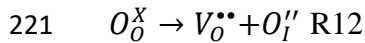
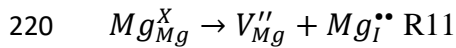
213 $3Mg_2SiO_4$ R6



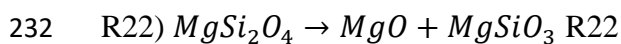
215 Anhydrous Extrinsic Reactions



219 Anhydrous Intrinsic Reactions



231 Buffer Reaction



233 Energies of these reactions are presented in Table 1 and Table S6. Despite using Kroger-Vink
 234 notation we allow the number of sites in forsterite to vary if forsterite is created or destroyed
 235 (such as in R23 and R24) as explained in Muir et al. (2020) but this has no noticeable effect on
 236 the results. Defects in $\{ \}$ brackets are charge pairs that are associated with each other, this is
 237 represented in our model by placing them on adjacent sites. For most charge pairs the energy
 238 gain from randomly placing them in the crystal is larger than the energy gain (due to
 239 electrostatics) from pairing them. This is explored in Table S7. There are three exceptions.
 240 $\{Ti_{Mg}^{2-}(2H)_{Si}''\}$ pairs have large binding energies (5-6 eV) and thus should always occur as pairs
 241 and are represented as such in our model (R4). $\{Al_{Mg}^i Al_{Si}'\}$ pairs and $\{2Al_{Mg}^{\bullet} V_{Mg}''\}$ triplets have
 242 middling binding energies and could occur as bound pairs/triplets in some situations. We allow
 243 for these systems to be both bound and unbound through reactions R9 and R10. We find that
 244 R9 does not happen in any of our explored conditions (as speculated in (Muir et al., 2020)) and
 245 all $\{2Al_{Mg}^{\bullet} V_{Mg}''\}$ triplets are unbound. We find that R10 happens moderately with $\{Al_{Mg}^i Al_{Si}'\}$
 246 bound pairs being anywhere from 1.01% to 99.81% of the $Al_{Mg}^i Al_{Si}'$ pairs with the remaining
 247 percentage being unbound. Lower temperatures, higher Al concentrations and pressures lead
 248 to more bound $\{Al_{Mg}^i Al_{Si}'\}$ pairs with water concentration having little effect. All reactions
 249 above have been written in a system where $MgSiO_3$ is present and numbers shall be presented
 250 as such. This can be converted to a system where MgO is present by using R22 in appropriate
 251 amounts. Al is placed initially as an unbound pair of Al_{Mg}^i and Al_{Si}' . Ti is initially placed as a
 252 4+ cation replacing Si (Berry et al., 2007b).

253 In this formulation water starts (arbitrarily) as $(2H)_{Mg}^x$ and then reacts until it reaches its
 254 thermodynamically favoured distribution across the various water sites. The possible sites for
 255 water are $(2H)_{Mg}^x$ (concentration of these sites shall be referenced as [HMg]), $(4H)_{Si}^x$ ([HSi]),
 256 $\{Ti_{Mg}^{2-}(2H)_{Si}''\}$ ([TiH]), $(1H)_{Mg}'$ ([1HMg]), H_{int} ([HFree]) and $(3H)_{Si}'$ ([3HSi]).

257

258 3.2 Pure Forsterite

259 We predict water in pure forsterite to produce 2 defects $(2H)_{Mg}^X$ and $(4H)_{Si}^X$. Two other
260 defects have been proposed in the literature and these are $(1H)'_{Mg}$ and H_{Int}^\bullet produced by R2
261 and R3. While there is evidence that $(1H)'_{Mg}$ is produced in the presence of ferric iron (Berry
262 et al., 2007a, Blanchard et al., 2017) there is no clear evidence for the production of $(1H)'_{Mg}$
263 and H_{Int}^\bullet in forsterite. We find these to be extremely minor products. In none of our runs did
264 the concentration of $(1H)'_{Mg}$ exceed 1×10^{-20} (the limit of detectability we set in our model) and
265 H_{Int}^\bullet never exceeded 1×10^{-7} defects/f.u. and 1×10^{-9} defects/f.u. in the absence of Al (Figure 1).
266 To confirm this we looked at R2 and R3 as isolated reactions occurring by themselves with no
267 other reactions to consider. R2 proceeding to the right is disfavoured by enthalpy and produces
268 no entropy gain and thus $(1H)'_{Mg}$ is never favoured to be produced over $(2H)_{Mg}^X$. R3
269 proceeding to the right is strongly disfavoured by enthalpy and strongly favoured by entropy
270 and thus occurs at small water contents. At 0 GPa (corrected) and 2000 K we find that H_{Int}^\bullet
271 exceeds $(2H)_{Mg}^X$ only when water content is < 0.2 wt. ppb. This is an extremely small water
272 content. Lower temperatures or higher pressures will decrease the concentration at which H_{Int}^\bullet
273 is favoured and the amount of H_{Int}^\bullet that is formed (see Table 2). Thus H_{Int}^\bullet and $(1H)'_{Mg}$ are
274 not substantially stable products in these systems and shall be ignored in the rest of this work.
275 In Kohlstedt (2006) exponents of water concentrations are derived based upon charge balance
276 conditions and we find that for any reasonable amount of water (above 1 ppb) the charge
277 balance condition is $[p^\bullet] = 2[H'_{Me}]$ under this scheme.

278 In pure forsterite either $(2H)_{Mg}^X$ or $(4H)_{Si}^X$ can be the dominant water product (Figure 1). High
279 temperature encourages the formation of $(2H)_{Mg}^X$ (Figure 2) as it increases the configurational

280 entropy (by having 2 defect sites to 1 for $(4H)_{Si}^X$), high water concentration stabilises $(4H)_{Si}^X$
281 (Figure 1, again due to entropy) and high pressure (Figure 3) encourages the formation of
282 $(4H)_{Si}^X$ as seen previously experimentally (Smyth et al., 2006, Xue et al., 2017, Withers and
283 Hirschmann, 2008, Mosenfelder et al., 2006). This is because R1 which produces $(4H)_{Si}^X$
284 eliminates a vacancy which are large and disfavoured by pressure. We plot the pressure at
285 which this occurs in Figure 4. Decreasing SiO_2 activity (by swapping enstatite for MgO)
286 increases $(2H)_{Mg}^X$ stability considerably but the mantle is more closely represented by an
287 enstatite buffer so from now on all of our results will be buffered by enstatite as presented in
288 the reactions above. For large amounts of water ($> \sim 520$ wt. ppm) $(4H)_{Si}^X$ is always the
289 dominant water product even at 2000 K and 0 GPa. In upper mantle conditions with low
290 amounts of water < 500 wt. ppm water should switch from $(2H)_{Mg}^X$ to $(4H)_{Si}^X$ at some
291 characteristic depth depending upon water content and temperature as shown in Figure 4.

292 A key variable in predicting water effects is the water exponent (r) generally defined as:

293 $[Defect] \propto f_{H_2O}^r$ Equation 4

294 In simple systems where each product can be described by a single equation (such as $(4H)_{Si}^X$
295 being solely produced by R1) and where configuration entropy is unimportant each product
296 can be described by a single number which should be relatively insensitive to pressure,
297 temperature and water concentration. In complex systems r will vary significantly with
298 condition. We examine this in our system in Table 3.

299 In our system we do not have water fugacity but we can instead determine

300 $[Defect] \propto [H_2O]_{bulk}^r$ Equation 5

301 All values of r in this study shall refer to that of Equation 5 rather than 4. While Equation 4
302 and 5 have occasionally been treated as the same in previous literature they are not as Equation

303 4 has additional mixing terms that are not present in Equation 5. For Equation 5 the dominant
 304 water defect (the species that provides the charge balance regime) in forsterite should have an
 305 r that trends towards 1 while the exponents of the other water species are (in a simple system)
 306 dependent on how the minor water species relate to the major species. For example in a simple
 307 system where $(2H)_{Mg}^X$ is the major product it will have an exponent of 1 and $(4H)_{Si}^X$ will have
 308 an exponent of 2 based on R1. Conversely where $(4H)_{Si}^X$ is the major product it will have an
 309 exponent of 1 and $(2H)_{Mg}^X$ will have an exponent of 0.5 in a simple system. This can be seen
 310 in Table 3 for the Ti and Al containing system where at 2000 K and 0 GPa the exponent for
 311 $(2H)_{Mg}^X$ is 1 and $(4H)_{Si}^X$ is 2 (a system charge balanced by $(2H)_{Mg}^X$) but at 10 GPa these values
 312 are 0.5 and 1 (a system charge balanced by $(4H)_{Si}^X$). The exponents for $(2H)_{Mg}^X$ and $(4H)_{Si}^X$
 313 as well as those of V_{Mg}'' and V_{Si}'''' always have a roughly 1:2 ratio because the Si vacancies are
 314 controlled by R1 and R14 respectively.

315 Our exponents were determined by fitting to:

316 $\ln[Defect] = a + r \ln[H_2O]_r$ Equation 6

317 where a is a variable and the results are presented in Table 3. We find that exponent values are
 318 quite variable and often do not have their ideal value. At low temperatures and high pressures,
 319 the exponents approach their ideal values but as temperature rises or pressure decreases the
 320 exponents are always above their ideal values due to configurational entropy which relatively
 321 increases in both of these cases. Exponents were measured in Tollans *et al.* 2017 where they
 322 found values of 2.5 for $(4H)_{Si}^X$, 1.1 for $(2H)_{Mg}^X$ and 0.9 for $\{Ti_{Mg}''(2H)_{Si}''\}$ using Equation 4
 323 instead of 5. These values are all slightly higher than the ideal values with deviations coming
 324 both from possible non-ideality of their NaCal fluid but also the presence of some
 325 configurational entropy will always raise exponents above their ideal values as shown here.
 326 Thus the water exponents r in real systems should be heavily dependent upon pressure,

327 temperature and chemical environment and can vary across common water ranges with
328 particularly large variations as the major hydrous product changes (Figure 1).

329 The presence of water will also have a large effect on the intrinsic defects of forsterite as shown
330 in Figure 5. In general the presence of water suppresses the formation of intrinsic defects.
331 This is because they form due to configurational entropy gains upon formation and these gains
332 are relatively decreased in the presence of water (or other extrinsic defects).

333 Each atom in Mg_2SiO_4 can have a vacancy or an interstitial defect. Mg vacancies (V_{Mg}'') and
334 Mg interstitials (Mg_i^{**}) are the most prominent extrinsic defects due to the favourability of R11
335 over other extrinsic reactions (Table 1 and S6). V_O^{**} is the next most prominent vacancy due to
336 R15 and then V_{Si}'''' due to R14. We find that V_{Si}'''' is produced by R14 and not by any of the
337 other V_{Si}'''' reactions which are higher in energy (Table S6). Thus the concentration of V_{Si}'''' is
338 proportional to the concentration of V_{Mg}'' which is a reactant in R14. Previous thermodynamic
339 models have used R13 as a base for V_{Si}'''' (Stocker and Smyth, 1978) and thus came to different
340 conclusions about the effect of various conditions on V_{Si}'''' but we find this to be extremely
341 unfavourable. No mechanism that we tested that produces O_i'' or Si_i^{****} was favourable and
342 thus the production of these defects was below the detection limit (1×10^{-20} defects/f.u.) and
343 likely far below this limit based on the extremely high energies of all reactions that produce
344 these interstitials. Thus we conclude Si and O interstitials are not present in forsterite to any
345 significant degree.

346 The effect of water on intrinsic defect exponents has been previously speculated in (Kohlstedt,
347 2006). Using speculations on the key defect producing reactions and the effect of water on K
348 they postulated that water has no effect on Si and Mg vacancies ($r=0$) in the charge balance
349 regime $[p^*] = 2[H'_{Me}]$. This was extended to O vacancies (Fei et al., 2016) which also had $r=0$.
350 We find, however (Table 3) that generally these products have negative exponents due to the

351 suppressive effect of water on their configurational formation entropy. The exponent of V''_{Mg}
352 is sometimes positive due to the effects of R3 which creates V''_{Mg} . While R3 only operates in
353 very small amounts relative to other water products it can still create V''_{Mg} at significantly
354 greater rates than are produced intrinsically. We cannot determine exponents for V''_{Si} directly
355 because the concentration of V''_{Si} is extremely low and often below our detection limit but as
356 the concentration of V''_{Si} is controlled entirely by R14 this exponent should be close to twice
357 that of V''_{Mg} .

358 We find significant deviations from the r values of literature ($r=0$) particularly in the presence
359 of Al and Ti. This is unsurprising as configurational entropy (which deviates from these perfect
360 values) will always be important for intrinsic defects as it is fundamental to their creation. All
361 the intrinsic defect forming reactions have high positive enthalpies meaning that they only
362 proceed forwards due to the configurational entropy gain of producing defects. Thus in most
363 scenarios the exponents for intrinsic defects will be heavily sensitive to configurational entropy
364 and deviate from their normal values. This means that when dealing with intrinsic defects their
365 exponents are particularly hard to extrapolate across temperature and pressure space and must
366 be measured at the desired conditions.

367 *The Effect of Al*

368 As shown in Figure 1 Al has no large effects on the distribution of water in forsterite. Some
369 $(3H)'_{Si}$ is produced through R5 and a very small amount of H'_{Int} through R7 though
370 considerably more than produced in pure forsterite. R6 is not significant and never produces
371 any detectible amounts of $(1H)'_{Mg}$. R8 can produce large amounts of V''_{Mg} leading to an
372 increase of the concentration of V''_{Mg} compared to pure forsterite but this effect is suppressed
373 by water and is negligible beyond ~5 wt. ppm water (Figure 5). The effects of this reaction are
374 explored in more detail in Muir et al. (2020). R5, R7 and R8 all increase the ratio of Al'_{Mg}/Al'_{Si}

375 from its initial value of 1 with this effect mostly controlled by R5. This ratio is plotted against
376 water concentration in Table S8. We find that these changes are generally small with Al_{Mg}^{\bullet}
377 usually being <0.1% larger than Al_{Si}' but at high temperatures, low pressures, low Al content
378 and high water content the $Al_{Mg}^{\bullet}/Al_{Si}'$ ratio can become significant and a strong measure of
379 water content in forsterite.

380 *The Effect of Ti*

381 Ti has a large effect on water distribution through the formation of $\{Ti_{Mg}^{\bullet}(2H)_{Si}''\}$ as R4 is very
382 favourable. As shown in Figure 1 and 3 at low pressures $\{Ti_{Mg}^{\bullet}(2H)_{Si}''\}$ can compete with
383 $(2H)_{Mg}^X$ to be the major product. Low temperatures (Figure 2) and high Ti concentrations
384 (Figure 6) favour $\{Ti_{Mg}^{\bullet}(2H)_{Si}''\}$ over $(2H)_{Mg}^X$ while pressure (Figure 3) and water
385 concentration have little effect (Figure 1). R4 is insensitive to pressure (Table 1) and thus with
386 increasing pressure $\{Ti_{Mg}^{\bullet}(2H)_{Si}''\}$ is disfavoured against $(4H)_{Si}^X$ similar to $(2H)_{Mg}^X$. This is
387 seen in Figure 4 where Ti makes only small changes to the pressure at which $(4H)_{Si}^X$ is
388 dominant.

389 Similar to Al the site of Ti is a measure of water content. As shown in Table S9 the $Ti_{Si}^X/Ti_{Mg}^{\bullet}$
390 ratio is roughly linear with water content for a fixed P, T and Ti concentration. The ratio varies
391 strongly and nonlinearly with P and T so fitting a universal law is complex and will have
392 overlapping points but inside a known P and T the water content can be solved. This provides
393 both a test of unknown water content if this ratio can be measured and a test of our model if
394 water content is known.

395 4. Discussion

396 *The distribution of water in the upper mantle*

397 Figure S4 shows the distribution of water along an upper mantle geotherm (Ono, 2008) (Table
398 S10) in a pure forsterite. $(4H)_{Si}^X$ is always favoured over $(2H)_{Mg}^X$ even with 10 wt. ppm water
399 because at low pressures (which favour $(2H)_{Mg}^X$) the temperature is also low which favours
400 $(4H)_{Si}^X$. As depth increases pressure increases and there is a sharp decline in [HMg]. While
401 there is an increase in [HSi] with depth this increase is negligible compared to the concentration
402 at 0 km and so in the absence of other defects [HSi] is steady throughout the upper mantle.

403 The presence of Al and Ti changes this picture. Figure 7 shows the distribution of these
404 products along the same geotherm but with Al and Ti added. The concentration of both Al and
405 Ti was set to a realistic distribution across the mantle using Equation 13 from De Hoog et al.
406 (2010) (values are given in Table S10) such that the concentration of Al and Ti decreases with
407 depth.

408 In the presence of Al and Ti we find that at shallow depths $\{Ti_{Mg}^{''}(2H)_{Si}^{''}\}$ is the most prominent
409 defect except with large amounts of water ($> \sim 500$ wt. ppm) when $(4H)_{Si}^X$ is the prominent
410 defect throughout the upper mantle. With increasing depth each of the 3 important hydrated
411 defects change in different ways. [HMg] initially increases slightly with depth (due to
412 increased temperature favouring $(2H)_{Mg}^X$ over $\{Ti_{Mg}^{''}(2H)_{Si}^{''}\}$), peaking at ~ 100 km for 10 wt.
413 ppm water, ~ 50 km for 100 wt. ppm water and 0 km for 1000 wt. ppm water, before decreasing
414 in concentration sharply beyond this point. [HTi] decreases throughout the upper mantle.
415 Initially [HTi] decreases slowly up to around the same point that [HMg] peaks before
416 decreasing sharply. [HSi] initially increases sharply with depth as the increased pressure
417 favours it over the other two defects before reaching a point where $(4H)_{Si}^X$ is the most
418 prominent defect and it becomes essentially unchanged with depth, mimicking the behaviour
419 seen in Ti and Al-free forsterite in Figure S4. The depth at which this change in behaviour
420 occurs is shown in Figure 8 and is ~ 200 km for 1 wt. ppm, ~ 150 km for 10 wt. ppm, ~ 100 km

421 for 100 wt. ppm and 0 km for 1000 wt. ppm water. Thus in shallower drier areas of the upper
422 mantle [HSi] increases sharply with depth but in wetter areas it is consistent with depth.

423 The changes between Figure 7 and S4 are induced by Ti and not by Al as demonstrated above.
424 The concentration of Ti in the sample is important only if the Ti concentration is low compared
425 to the water concentration in which case $\{Ti_{Mg}''(2H)_{Si}''\}$ will saturate and be lower than
426 predicted here. Figure S5 shows the same plot as Figure 7 but with a constant (500 wt. ppm)
427 amount of TiO₂ and Al₂O₃. Figure S5 and 7 are nearly identical. This is because at shallow
428 depths, where Ti makes a large difference to the distribution of water, there is large amounts
429 of Ti in both our geological distribution in Fig 7 and in our fixed Ti-rich trace in S5. At deep
430 depths where there is large amounts of Ti in Figure S5 and small amounts in the geological
431 distribution in Figure 7 $(4H)_{Si}^X$ dominates regardless of Ti concentration. Thus in shallow and
432 dry areas of the upper mantle Ti concentration (relative to water concentration) is important
433 but in deep and/or wet areas of the upper mantle Ti concentration levels are irrelevant for the
434 main distribution of water in forsterite. Figure S5 contains the highest level of Ti that is likely
435 present in the upper mantle and real samples are likely somewhere between this and Figure 7.
436 Thus $(4H)_{Si}^X$ is likely always the dominant water product in mantle forsterite and steady
437 throughout the upper mantle except for the shallowest, driest and most Ti rich forsterites.

438 *[HMg]*

439 Increasing the concentration of $(2H)_{Mg}^X$ will primarily have effects on the diffusion of Mg (Fei
440 et al., 2018), the diffusion of hydrogen and the conductivity in regions above ~900 C and with
441 high water concentrations- ie most of the upper mantle (Demouchy and Bolfan-Casanova, 2016,
442 Demouchy and Mackwell, 2006, Yoshino et al., 2017, Novella et al., 2017). We find that with
443 small amounts of water (with some Ti and Al) [HMg] initially rises and then falls sharply after

444 a depth defined by temperature, water and Ti concentration. With large amounts of water
445 [HMg] decreases slowly around the first 100 km of the upper mantle and then quickly.

446 Under young oceanic plates conductivity increases on the order of a magnitude have been seen
447 peaking at around 70-120 km (Baba et al., 2006, Baba et al., 2010). If these regions contain
448 water this conductivity spike could be explained by $(2H)_{Mg}^X$. The conductivity increase seen
449 in these regions is also strongly anisotropic which can also be explained by an increase of
450 $(2H)_{Mg}^X$ as increasing the Mg diffusion rate by adding vacancies should lead to anisotropic
451 diffusion and thus conduction.

452 In the general upper mantle conductivity either increases sharply up to 100 km depth and then
453 slowly afterwards in oceanic mantle or continually increases at similar rates in continental
454 mantle (Sun et al., 2019). While conductivity will generally increase as you descend into the
455 mantle simply due to the increased temperature if conductivity in this region is tied to Mg
456 diffusion rates which are tied to water one would expect, based on this work, a large decrease
457 in conductivity with depth which is not observed in reality.

458 There are three reasons why such a signal may not be observed. First the relationship of
459 $(2H)_{Mg}^X$ to Mg diffusion rates and conductivity may not be straightforward. A relatively
460 immobile $(2H)_{Mg}^X$ could explain why there is no large decrease in conductivity with depth.
461 Alternatively Mg diffusion in forsterite might not be the controlling factor for forsterite in these
462 conditions with polaron or grain boundary diffusion or other mechanisms actually being
463 dominant. Second the increased temperature of the deep upper mantle which will increase
464 conductivity may outweigh the decreases caused by a shrinking [HMg]- the diffusivity of
465 $(2H)_{Mg}^X$ needs to be known to address this point. Third it may be that Mg diffusion controls
466 the conductivity of forsterite but that the upper mantle is very dry. A dry upper mantle would

467 only have small changes to Mg diffusion regardless of the relative prominence of $(2H)_{Mg}^X$ and
468 thus no conductivity decreases with depth.

469 *[HSi]*

470 Increasing the concentration of $(4H)_{Si}^X$ will have large effects as Si is the slowest diffusing
471 species in olivine (Chakraborty, 2010) and thus is assumed to control its diffusion-mediated
472 creep, both in diffusion creep and dislocation creep regimes where they are climb limited (see
473 Demouchy and Bolfan-Casanova (2016) for a review). Thus adding water to forsterite,
474 particularly at high pressure, should increase its creep rate and cause it to weaken. This
475 “hydrolytic weakening” has been observed in both diffusion and dislocation creep regimes
476 (Mei and Kohlstedt, 2000a, Mei and Kohlstedt, 2000b, Karato et al., 1986, Demouchy et al.,
477 2012, Girard et al., 2013a, Tielke et al., 2018, Jung and Karato, 2001, Hirth and Kohlstedt,
478 2003, Mackwell et al., 1985), as has an increase in the silicon diffusion rate (Costa and
479 Chakraborty, 2008, Fei et al., 2013) with these two mechanisms hypothesised as linked (Fei et
480 al., 2016). The strain rate of forsterite has been found to increase in the presence of water from
481 around half an order of magnitude (Mei and Kohlstedt, 2000a, Mei and Kohlstedt, 2000b, Fei
482 et al., 2013, Girard et al., 2013b, Tielke et al., 2018, Demouchy et al., 2012, Umemoto et al.,
483 2011) to a couple of orders of magnitude (Costa and Chakraborty, 2008, Karato et al., 1986,
484 Jung and Karato, 2001) with these differences often explained by experimental differences in
485 strain rates, compositions and water content with grain boundary water likely an important
486 confounder of results. The two works at the highest pressures (4-8 GPa (Fei et al., 2013, Girard
487 et al., 2013a)) where *[HSi]* should be the largest found the lowest weakening which could be
488 evidence that either *[HSi]* is not important in Si diffusion or that Si diffusion is not important
489 in the rheological strength of forsterite (which would also explain the difference between direct
490 strength measurements and those from Si diffusion measurements) but may be evidence that
491 other studies have overestimated the weakening effects.

492 Determining the water exponent of hydrolytic weakening will give insight into its weakening
 493 mechanism. The exponent of water's effect has been measured as 1/3 (Fei et al., 2013), 0.2-1
 494 (Costa and Chakraborty, 2008), ~1.2 (Hirth and Kohlstedt, 2003, Tielke et al., 2018) and 0.2
 495 (Mackwell et al., 1985) though in all cases the experimental data is scattered and could be
 496 plausibly fit with different exponents. In Fei et al. (2016) an exponent of 1/3 was explained
 497 for Si diffusion by co-diffusion of Si and O using the exponents of Kohlstedt (2006) and a
 498 charge balance regime of $[(OH)_{\dot{O}}] = 2[V_{Mg}^{\prime\prime}]$ with $V_{Si}^{\prime\prime\prime\prime}$ having an exponent of 2/3 and with
 499 $(4H)_{Si}^X$ being immobile. We find this unlikely for a few reasons. We find that the charge
 500 balance regime is either $[p^{\bullet}] = 2[H'_{Me}]$ or $[p^{\bullet}] = 4[H'_{Si}]$ and thus $V_{Si}^{\prime\prime\prime\prime}$ will be either
 501 unchanged by water content ($r=0$ in the ideal case) or somewhat decreased due to entropy
 502 concerns (we find r for $V_{Si}^{\prime\prime\prime\prime}$ to be ~0- -0.5 in the conditions of the experiment 8 GPa, 1600-
 503 1800 K). Thus an immobile $(4H)_{Si}^X$ would lead to a decrease in Si diffusion rates with water.
 504 Even in the limit of the charge balance $[(OH)_{\dot{O}}] = 2[V_{Mg}^{\prime\prime}]$ the measured exponent of 1/3 is
 505 against $[H_2O]_{\text{bulk}}$ rather than water fugacity (Equation 5 rather than 4) and thus the perfect
 506 exponent for $V_{Si}^{\prime\prime\prime\prime}$ would be 2 and not 2/3. If $(4H)_{Si}^X$ is the dominant water structure and $[p^{\bullet}] =$
 507 $4[H'_{Si}]$ is the charge balance in these products as we predict then the exponent of both $V_{Si}^{\prime\prime\prime\prime}$ and
 508 $V_{O}^{\bullet\bullet}$ should be 0 in the ideal case and that of $(4H)_{Si}^X$ should be 1 with the actual exponent of
 509 $V_{Si}^{\prime\prime\prime\prime}$ and $V_{O}^{\bullet\bullet}$ being slightly negative. Determining the water exponent of Si diffusion is
 510 impossible in this work without knowing the diffusivity of dry and wet Si vacancies but a Si
 511 diffusion exponent of ~1/3-2/3 at high pressure (where the $(4H)_{Si}^X$ exponent is ~1) or ~1.2 at
 512 lower pressures (where the $(4H)_{Si}^X$ exponent is ~2) makes sense if Si diffusion is a mixture of
 513 these two species as it would place the exponent roughly halfway between these two species.
 514 Thus we propose that the water exponent of Si diffusion is variable and is low (~1/3) at high
 515 pressure but higher at low pressure (<~1 GPa depending upon temperature and water content).

516 If Si diffusion is responsible for weakening of forsterite then the same exponent should also
517 hold for olivine strength.

518 Such an effect has been seen in olivine creep strength in Karato and Jung (2003) where it was
519 observed that in wet olivine creep strength decreases rapidly with pressure below ~1 GPa but
520 slowly above this. This is evidence of a changing exponent at around 1 GPa which makes
521 sense if creep rate is tied to Si diffusion which is tied to [HSi] as around 1 GPa you change
522 from a $(2H)_{Mg}^X$ dominated region to one dominated by $(4H)_{Si}^X$ and change the exponent of
523 $(4H)_{Si}^X$ from 2 to 1.

524 We predict such changes to occur in the upper mantle. As can be seen in Figure 8 there are
525 two regions for [HSi] in the upper mantle reflective of these two charge balance regions. In
526 the shallow upper mantle and in drier rocks there is a region of sharp increase in [HSi] with
527 depth, this is a region where $(2H)_{Mg}^X$ or $Ti_{Mg}^{..}(2H)_{Si}''$ dominates. In this region there should
528 be sharp increases in [HSi] with depth and thus large changes in olivine strength with depth.
529 For 100 wt. ppm water [SiH] increases by over an order of magnitude over the first 150 km,
530 for 10 wt. ppm water [SiH] increases by 2.5 orders over the first 200 km of the upper mantle
531 and olivine strength should lower accordingly. The second region is one where $(4H)_{Si}^X$ is the
532 dominant product and in this region [HSi] is nearly insensitive to depth. It increases slightly
533 with depth in all cases but this change is so small as to be negligible. Across this region the
534 strength of wet forsterite should be fixed with depth. This region starts earlier in the mantle
535 with more water (~200 km with 10 wt. ppm, ~150 km with 100 wt. ppm, ~0 km with 1000 wt.
536 ppm) such that very wet crystals should have consistent strength throughout the upper mantle.
537 These results suggest, therefore, that drier shallower olivines could have strengths that vary by
538 orders of magnitude with depth and that olivine cannot be treated as a structure with a fixed

539 strength throughout the upper mantle unless it is very wet such that [HSi] does not vary with
540 depth or extremely dry such that water does not change the strength at all.

541

542 In conclusion we find that water distribution in lower mantle forsterite is mainly a function of
543 depth. Lower water concentrations and higher temperatures favour $(2H)_{Mg}^X$ while higher Ti
544 concentrations favour $\{Ti_{Mg}^{2+}(2H)_{Si}''\}$ but pressure overwhelmingly favours $(4H)_{Si}^X$ and this
545 becomes the key factor descending into the lower mantle. In drier rocks $(2H)_{Mg}^X$ or
546 $\{Ti_{Mg}^{2+}(2H)_{Si}''\}$ can be the dominant water defect and peak in concentration around 100-150 km
547 suggesting a maximum Mg diffusion rate and conductivity around this depth. In these drier
548 rocks [HSi] increases steadily across this range of depths and thus the rocks should become
549 weaker as they increase in depth. In very wet rocks $(4H)_{Si}^X$ is the dominant water carrying
550 phase throughout and thus there should be consistent Si diffusion rates and strength throughout
551 the upper mantle. Water in forsterite is highly sensitive to the environmental conditions and
552 so universal laws are likely to fail except outside the conditions in which they were created.

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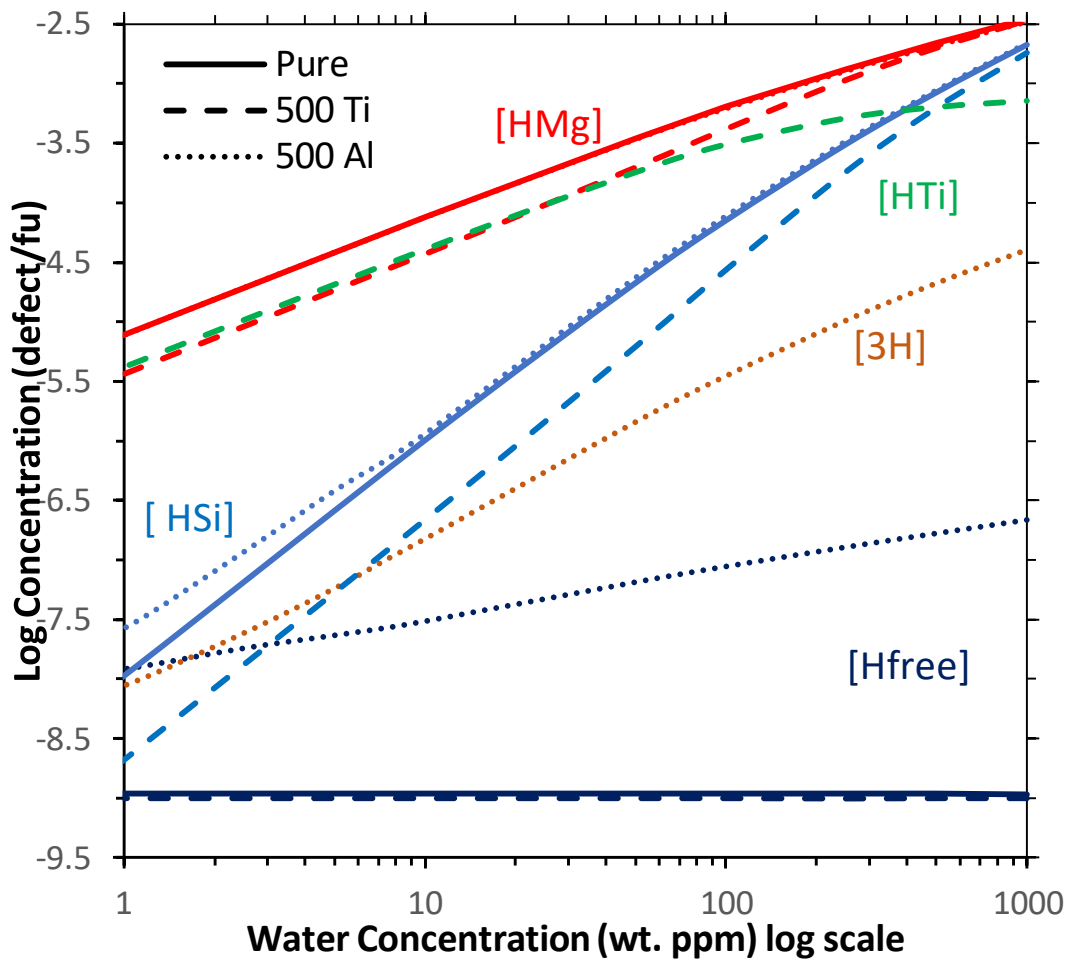
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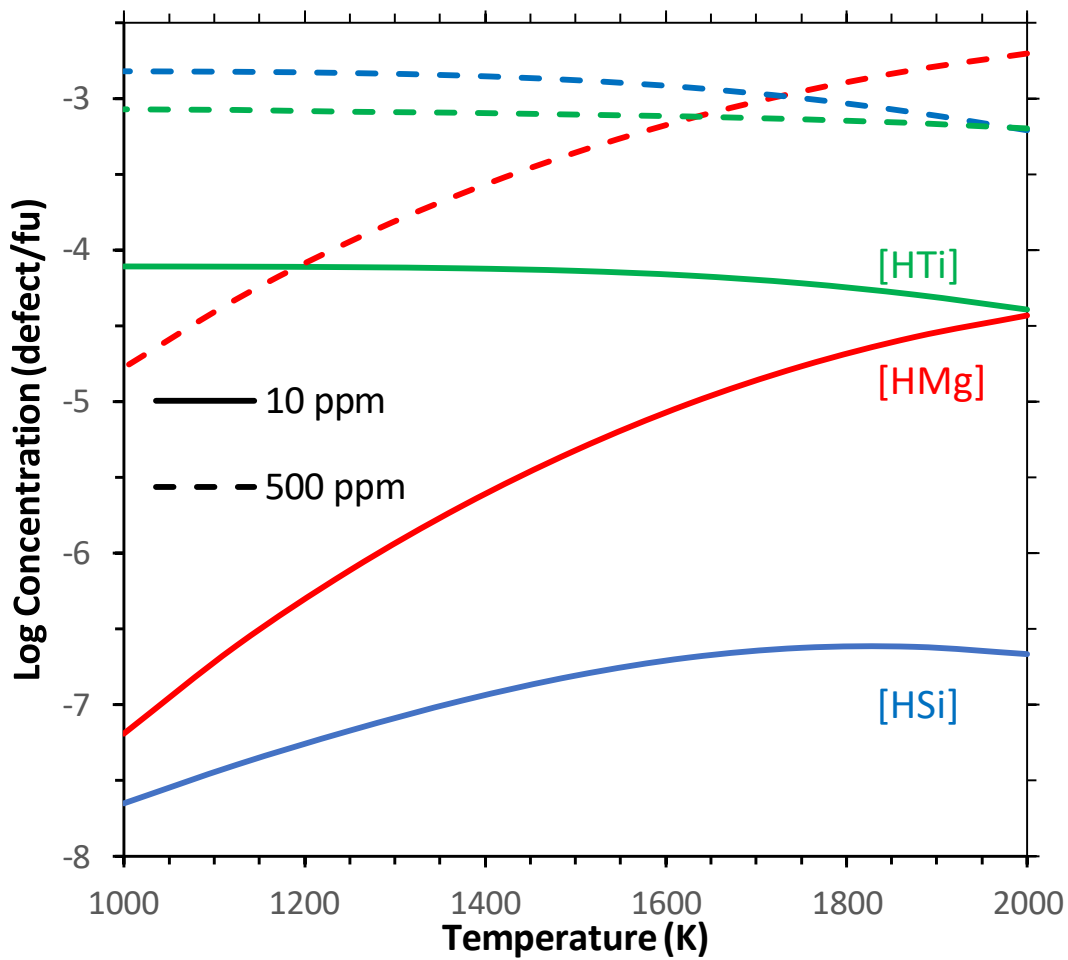
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719 Figure 1: Distribution of products at 2000 K and 0 GPa (corrected) as a function of water
 720 content (vs temperature is shown in Figure 2 and vs pressure in Figure 3). Different colours
 721 represent different defects and lines different systems (solid line= pure forsterite, dashed
 722 line=forsterite+ 500 wt. ppm Al_2O_3 , dotted line forsterite+500 wt. ppm TiO_2).
 723 Concentrations are defects/f.u. so [Si] has twice as much hydrogen as [Mg] with an
 724 equivalent concentration. [Hfree] is nearly identical with and without Ti. [HMg] is identical
 725 at this scale for pure and Al-containing forsterite. With increasing water [Si] is favoured. A
 726 high pressure graph (10 GPa corrected) is shown in Figure S1 which has very similar trends.

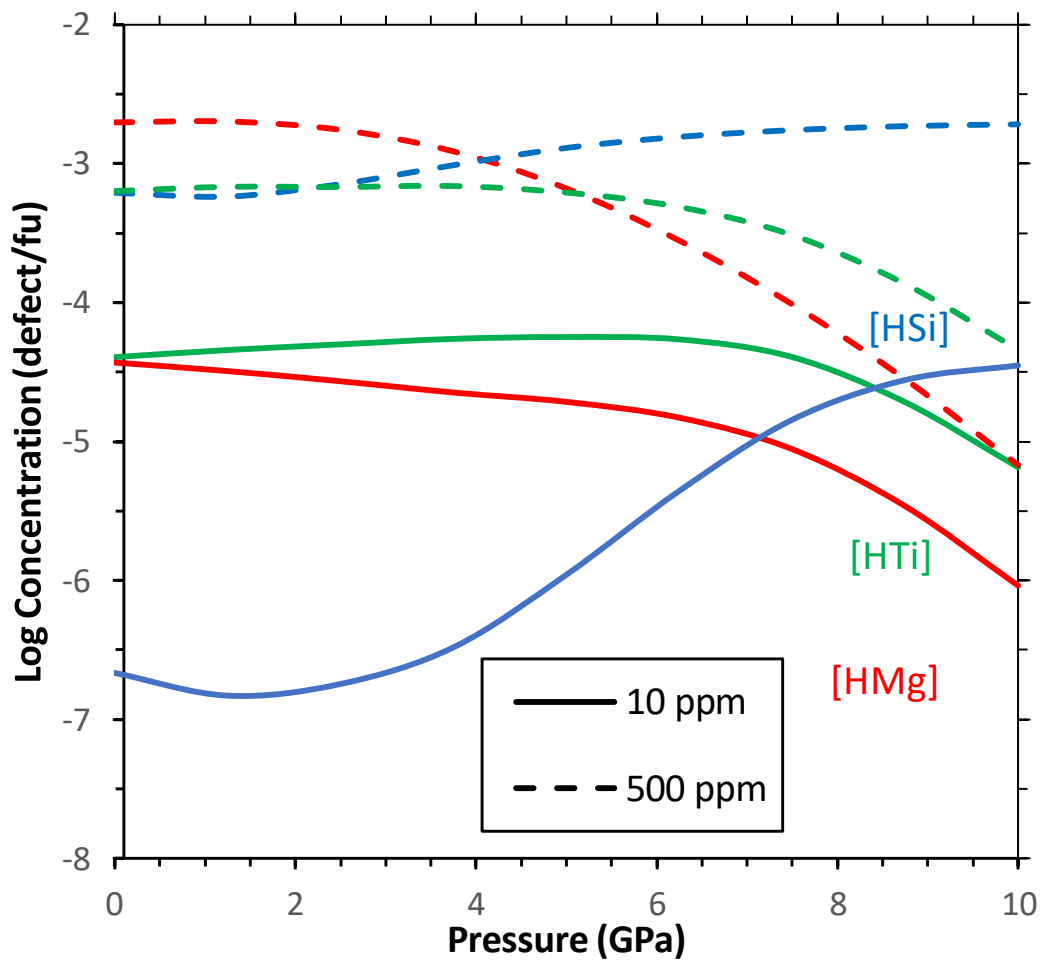
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729 Figure 2: Distribution of the 3 major products as a function of temperature at 0 GPa
 730 (corrected) with 500 wt. ppm Al_2O_3 and TiO_2 with 2 different water contents (10 wt. ppm=
 731 solid lines, 500 wt. ppm dashed lines). The same graph at 10 GPa is shown in Figure S2 and
 732 for pure forsterite in S3 though trends are similar in both cases just with changes in absolute
 733 values.

734



Figure

3: Distribution of the 3 major products as a function of pressure at 2000 K with 500 wt. ppm Al₂O₃ and TiO₂ with 2 different water contents (10 wt. ppm= solid lines, 500 wt. ppm dashed lines). Pressure increases [HSi] but this effect decreases with water content as [HSi] becomes the most prominent defect at all pressures (see Figure 4). [HMg] heavily decreases with pressure, [HTi] increases slightly with pressure and then heavily decreases.

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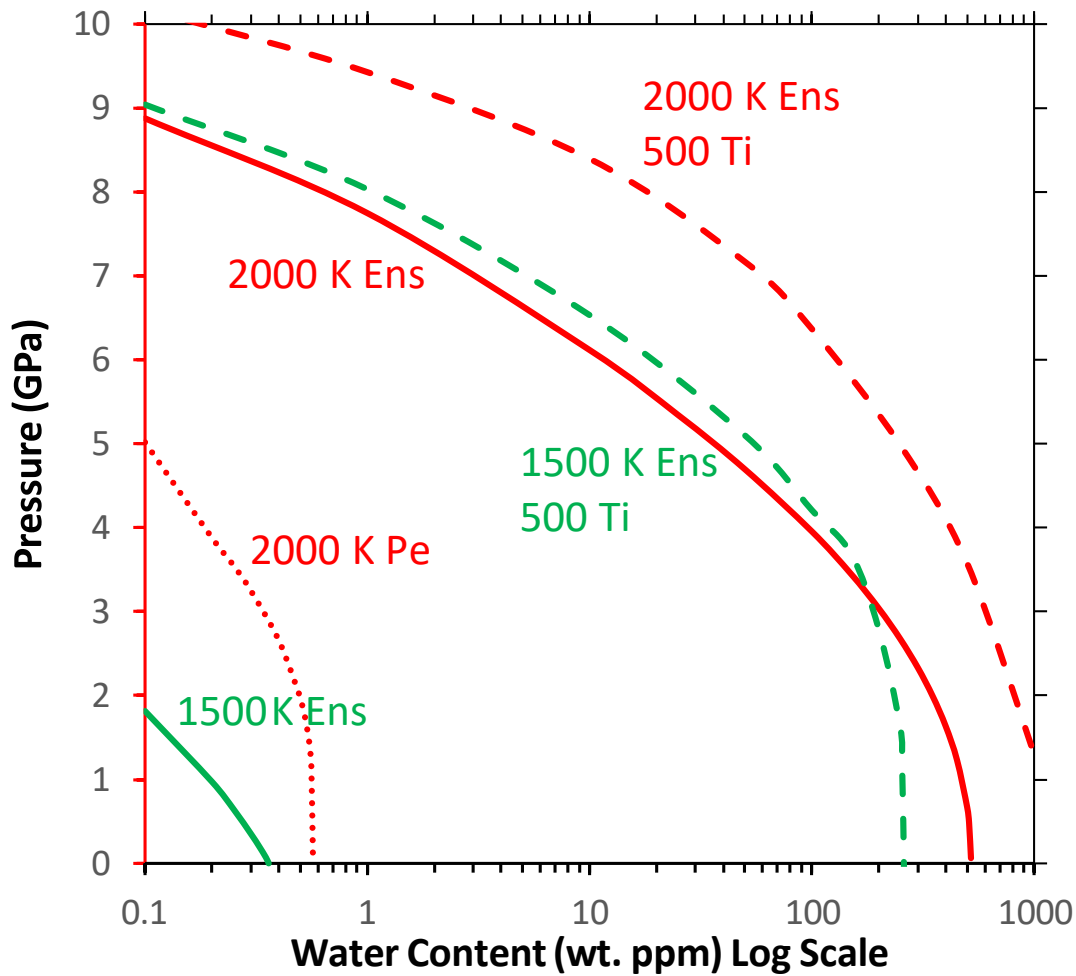
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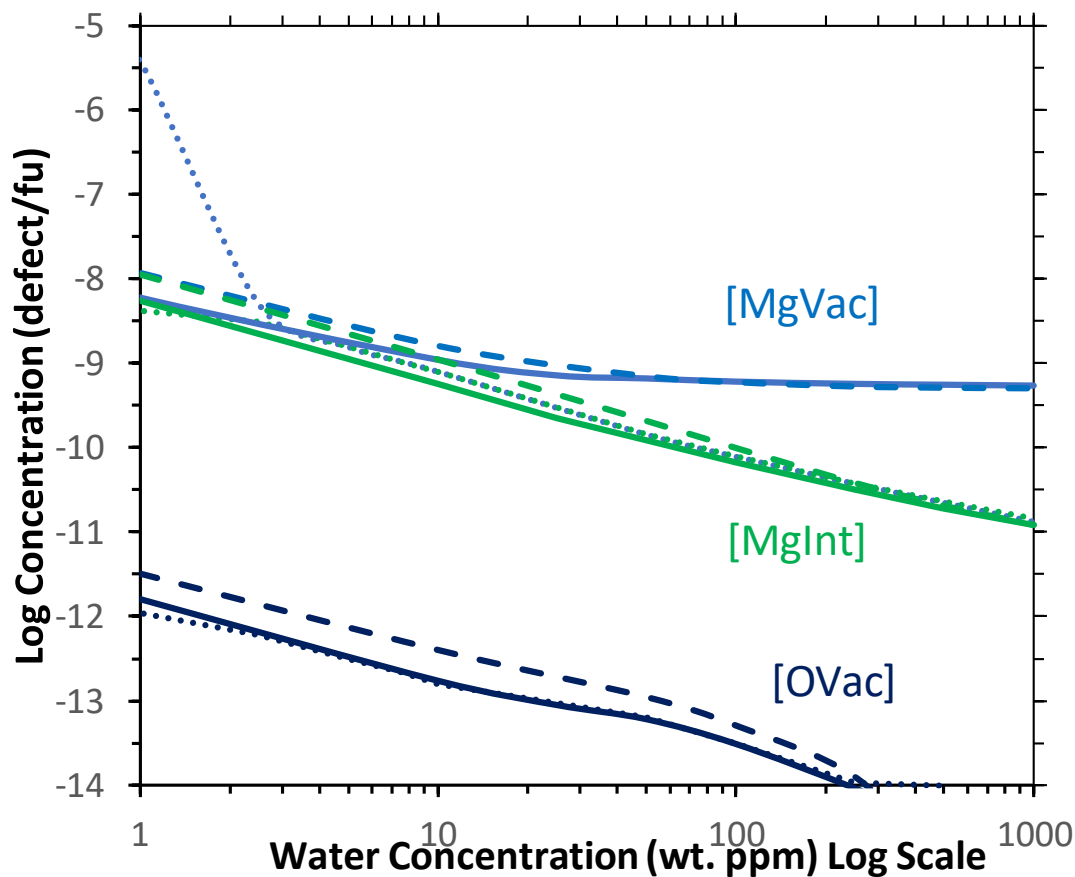
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745 Figure 4: The crossover pressure as a function of water at fixed T from water being mostly in
 746 $(2H)_{Mg}^x$ and $\{Ti_{Mg}^{2+}(2H)_{Si}^{2-}\}$ to being mostly in $(4H)_{Si}^x$ (lowest pressure at which $(4H)_{Si}^x$
 747 contains over half the water in the system). Shown are a pure forsterite buffered by enstatite
 748 (solid line), periclase (dotted line) and a forsterite containing 500 wt. ppm TiO₂ buffered by
 749 enstatite (dashed line) with colour representing temperature (red=2000, green=1500 K). For
 750 1500 K in a pe buffered Ti-free system $(4H)_{Si}^x$ contains the majority of the water even at 0
 751 GPa as with 1000 K for all conditions.



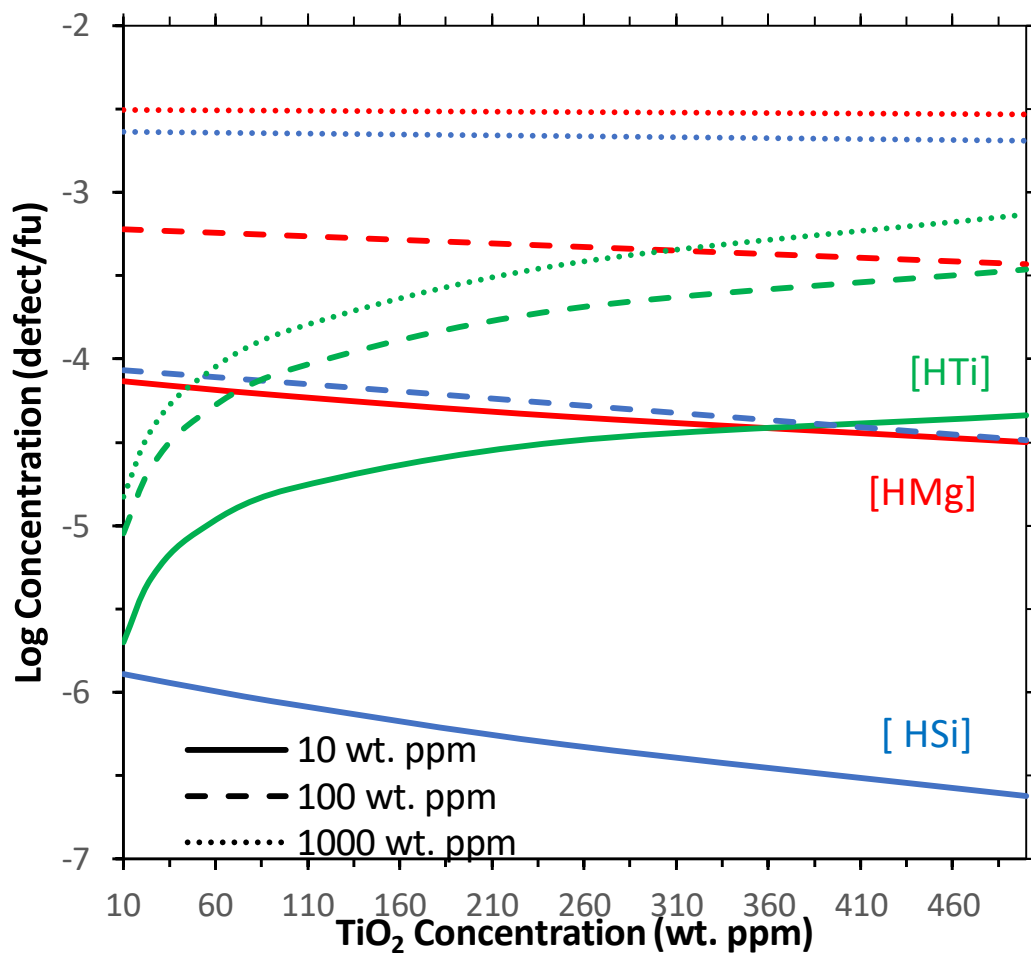
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753 Figure 5: Plot of the three major intrinsic defects as a function of water concentration at 2000
 754 K and 0 GPa (corrected) with three different crystal chemistries (solid line=pure forsterite,
 755 dashed line= 500 wt. ppm TiO₂, dotted line= 500 wt. ppm Al₂O₃). The only major difference
 756 induced by crystal chemistry is Al induces extra V''_{Mg} due to R8 but this effect is suppressed
 757 by high levels of water. The absolute value of these concentrations is less constrained than
 758 for intrinsic defects as their concentration is much smaller but the trends with water
 759 concentration are better constrained.

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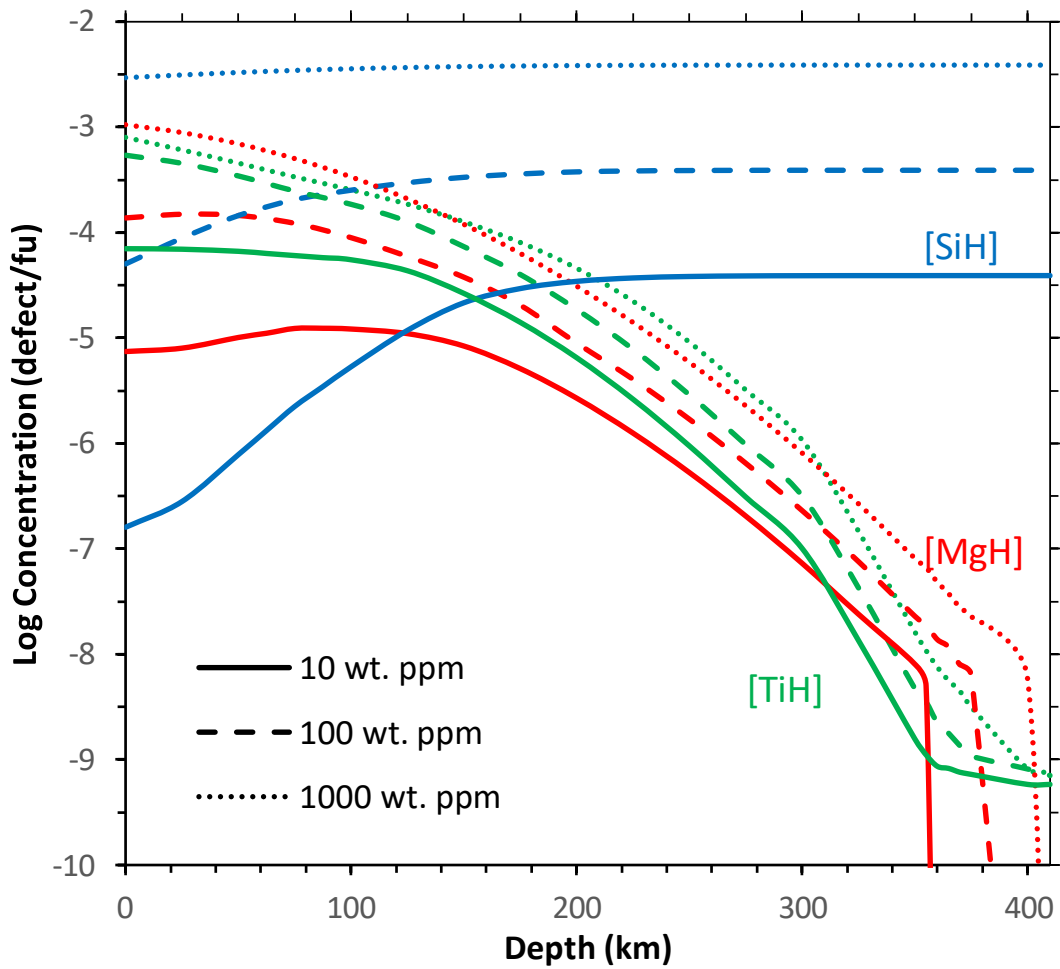
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764 6: Change in the concentration of the three major defects as a function of Ti content at 2000
 765 K and 0 GPa (corrected) and with different amounts of water (10 wt. ppm solid line, 100
 766 dashed line, 1000 dotted line).

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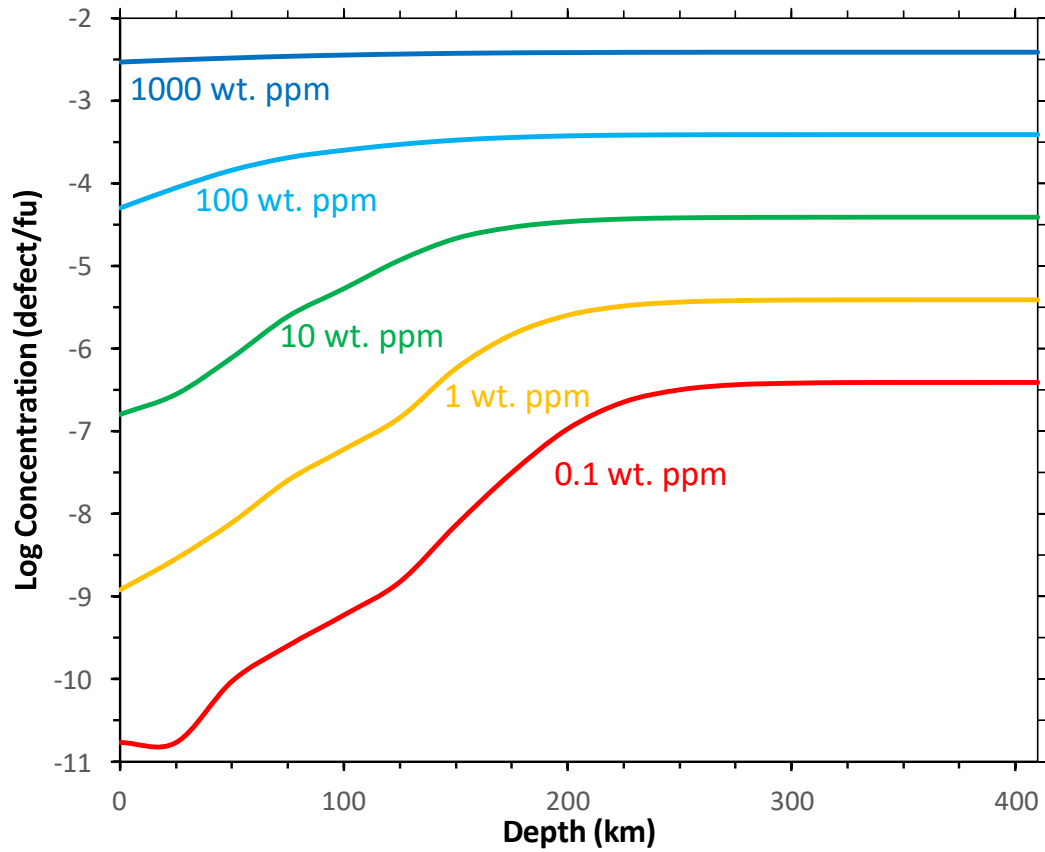


769

770 Figure 7: Plot of the distribution of the three major products along a geotherm with
 771 geological distribution of Al and Ti (Table S8) with three different water concentrations (10
 772 wt. ppm=solid lines, 100=dashed lines, 1000=dotted lines). For a system with no Ti and Al
 773 see Figure S4 and for one with fixed Ti and Al see Figure S5. The general trend is that of
 774 increasing $(4H)_{Si}^X$ while $(2H)_{Mg}^X$ increases and then decreases.

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776



777

778 Figure 8 As Figure 7 but just showing the values for [HSi] with different total water
 779 concentrations. With decreasing water [HSi] has a larger increase in concentration over
 780 shallower depths.

781

782

| | 0 GPa | | | 5 GPa | | | 10 GPa | | |
|-----|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| | 1000 K | 1500 K | 2000 K | 1000 K | 1500 K | 2000 K | 1000 K | 1500 K | 2000 K |
| R1 | -1.337 | -2.139 | -3.376 | -1.336 | -2.119 | -3.672 | -1.337 | -1.794 | -3.413 |
| R2 | 0.585 | 0.564 | 0.564 | 0.585 | 0.564 | 0.564 | 0.585 | 0.565 | 0.565 |
| R3 | 6.639 | 7.772 | 8.554 | 6.891 | 8.700 | 9.954 | 7.142 | 9.627 | 11.354 |
| R4 | -1.031 | -1.169 | -1.281 | -1.045 | -1.183 | -1.296 | -1.006 | -1.150 | -1.272 |
| R5 | -0.421 | -0.765 | -1.071 | -0.282 | -0.585 | -0.871 | 0.021 | -0.240 | -0.513 |
| R6 | 1.157 | 1.227 | 1.142 | 1.099 | 1.211 | 1.124 | 1.071 | 1.248 | 1.178 |
| R7 | 4.278 | 4.464 | 4.472 | 4.223 | 4.440 | 4.388 | 4.207 | 4.537 | 4.490 |
| R8 | 2.121 | 2.387 | 2.560 | 2.140 | 2.603 | 2.842 | 2.100 | 2.705 | 3.023 |
| R11 | 5.960 | 6.375 | 6.918 | 5.661 | 6.180 | 6.877 | 5.368 | 5.939 | 6.747 |
| R22 | 0.270 | 0.239 | 0.231 | 0.282 | 0.254 | 0.258 | 0.298 | 0.269 | 0.278 |

783 Table 1: Reaction energies (in eV/f.u) for the hydrated defect reactions (R1-R7) and some
784 other important reactions as a function of pressure and temperature. All other reactions are
785 shown in Table S6.

786

787

788

| P Corrected (GPa) | T (K) | Water Conc (wt. ppm) | log 2*[2H] | log [Hint] |
|-------------------|--------|----------------------|------------|------------|
| 0 | 1000 K | 0.001 | -7.80 | -15.95 |
| | | 1 | -7.30 | -15.95 |
| | | 1000 | -6.80 | -15.95 |
| 0 | 1500 K | 1 | -6.57 | -11.66 |
| | | 10 | -6.06 | -11.68 |
| | | 100 | -5.56 | -11.65 |
| 0 | 2000 K | 1 | -5.51 | -9.24 |
| | | 10 | -4.93 | -9.24 |
| | | 100 | -4.41 | -9.24 |
| 10 | 2000 K | 1 | -7.94 | -14.78 |
| | | 10 | -7.41 | -14.78 |
| | | 100 | -6.91 | -14.48 |

789 Table 2: Concentration (log defect/f.u.) of 2*[2H] and [Hint] (so that they have equal
790 amounts of hydrogen) as a function of pressure and temperature in a system with only 1
791 reaction R3. As can be seen by comparing these values to those in Figure 1 the introduction
792 of other reactions lowers [Hint] except for R7 which raises it a lot. [Hint] is always a lot
793 smaller than [2H] except for extremely small water contents.

794

795

| | | | [HMg] | [HSi] | [HTi] | $[V''_{Mg}]$ | $[Mg_i^{**}]$ | $[V_{\rho}^{**}]$ | $[V_{Si}^{****}]_{proj}$ |
|--|--------|--------|-------|-------|-------|--------------|---------------|-------------------|--------------------------|
| Pure | 5 GPa | 2000 K | 0.82 | 1.63 | n/a | 0.00 | -0.14 | -0.84 | -0.29 |
| | | 1500 K | 0.60 | 1.19 | n/a | -0.01 | -0.01 | 0.00 | -0.01 |
| | | 1000 K | 0.50 | 1.01 | n/a | -0.01 | -0.01 | 0.00 | -0.01 |
| | 15 GPa | 2000 K | 0.50 | 1.00 | n/a | 0.29 | -0.49 | -0.49 | -0.99 |
| | | 1500 K | 0.50 | 1.00 | n/a | 0.26 | 0.13 | 0.00 | 0.26 |
| | | 1000 K | 0.50 | 1.00 | n/a | 0.25 | 0.34 | 0.00 | 0.69 |
| TiO ₂ = 500 ppm Al ₂ O ₃ = 500 ppm | 5 GPa | 2000 K | 0.98 | 1.96 | 0.61 | 0.51 | -0.56 | 0.00 | -1.12 |
| | | 1500 K | 1.08 | 2.12 | 0.49 | 0.56 | -0.82 | -0.80 | -1.60 |
| | | 1000 K | 1.37 | 2.65 | 0.48 | 0.65 | -1.40 | -1.51 | -2.70 |
| | 15 GPa | 2000 K | 0.51 | 1.02 | 0.49 | 0.26 | -0.53 | -0.50 | -0.39 |
| | | 1500 K | 0.50 | 1.00 | 0.47 | 0.25 | -0.19 | -0.13 | -1.06 |
| | | 1000 K | 0.50 | 1.00 | 0.46 | 0.24 | -0.02 | 0.00 | -0.04 |

796 Table 3: The water exponent r determined for each of these systems by fitting equation 5
797 between 10-1000 wt. ppm water. Below 10 wt. ppm water there are sometimes sharp
798 changes in concentration which can strongly distort the exponent. An exponent for V_{Si}^{****}
799 cannot be reliably determined because it's concentration is small but its concentration is
800 overwhelmingly controlled by R14 and thus its exponent should be roughly double that of
801 V''_{Mg} similarly to how [HSi] is roughly twice [HMg] because it is controlled by R1.

802 These exponents can be converted into those of equation 4 by assuming an exponent for one
803 of the products. If we assuming [HMg] has a water exponent in Equation 4 then the Equation
804 5 exponents of the other products can be determined by dividing their exponents by the
805 exponent of [HMg] (first column).

806

807

808

809 **Supplementary Methods for “the distribution of hydrogen in Al and Ti-containing**
810 **forsterite: A thermodynamic model”**

811

812 In this section we go into more detail about how we determine energy of different
813 configurations, the different arrangements involved in each defect, the different assumptions
814 involved in our calculation and how our thermodynamic minimiser works.

815

816 *Determining the energy of defective systems*

817 27 defect forming reactions are presented in the text. We need to find the concentration of
818 defects that provides the lowest possible energy. Each reaction is assigned a reaction vector
819 ($x_1 \dots x_{27}$) between 0 and 1 which determines how far each reaction proceeds to the right
820 between all reactants and all products. For any combination of x_1 - x_{27} we can solve for the
821 free energy and the thermodynamic equilibrium is where this free energy is minimised. Solving
822 for the free energy consists of two parts determined as the non-configurational energy and the
823 configurational entropy section:

824 $\Delta G = \sum_i \Delta E \times x_i - TS_{confa}$ Equation S1

825 The first half of Equation S1 involves multiplying the energy of each reaction at the
826 appropriate P and T (see Table 1) by its reaction vector to obtain the non-configurational
827 entropy. The second half of Equation S1 involves finding the configurational entropy term
828 S_{confa} for any collection of defects.

829 1.1) *Configurational Entropy*

830 The configurational entropy term S_{confa} has many different components and is not
831 straightforward to determine. In short we used the Gibbs entropy formula:

832 $S = -k_B \sum_j p_j \ln p_j$ Equation S2

833 Where k_B is the Boltzmann constant, j represents a specific configuration of defects and p_j the
 834 probability that configuration occurs. A configuration refers to how defects are arranged across
 835 the supercell with a set concentration.

836 The probability of any specific configuration occurring is:

837
$$p_j = \frac{1}{Z} e^{(-U_j/k_B T)} \text{ Equation S3}$$

838 Where U_j is the internal energy of each configuration. Z in Equation S3 is the canonical
 839 partition function:

840
$$Z = \sum_i e^{(-U_j/k_B T)} \text{ Equation S4}$$

841 Strictly speaking S3 and S4 should be calculated with G_j (the free energy of each
 842 configuration) rather than U_j (the internal energy of each configuration). This was an
 843 approximation made to allow us to calculate the energy of many different configurations
 844 quickly as U is much easier to calculate the G . We shall discuss this approximation later. We
 845 also do these calculations in the dilute limit with all systems fixed to the forsterite unit cell.
 846 This means PV terms do not vary reducing H_j terms to U_j .

847 At this point we shall define a scheme to group the configurations and bring them down to a
 848 calculable number. We shall thus define a configuration as a state where each of the defects of
 849 each type is confined to a single type of site. This can be imagined by having a single defect
 850 of each type and so the different configurations simply change which site each defect occupies.
 851 With our assumption that defects are independent every configuration with the defects confined
 852 to a single site is identical and configurations where defects occupy multiple sites are included
 853 by the partitioning function. V''_{Mg} , $(1H)'_{Mg}$, $(2H)^X_{Mg}$ and Al_{Mg} were confined to M1 and M2
 854 sites, V''''_{Si} , Ti^X_{Si} , $(4H)^X_{Si}$, $(3H)'_{Si}$ and Al'_{Si} to Si sites, $Mg_i^{\bullet\bullet}$ to M1 and I2 sites, $V_o^{\bullet\bullet}$ and H_{Int} to
 855 O1, O2 and o3 sites and O_i'' and $Si_i^{\bullet\bullet\bullet}$ to I1, I2 and T1-T5 sites (which are defined in (Muir et
 856 al., 2020)). $\{Ti_{Mg}(2H)''_{Si}\}$, $\{2Al_{Mg}V''_{Mg}\}$ and $\{Al_{Mg}Al'_{Si}\}$ were calculated as pairs/trios with

857 each element of the defect confined to a next or second-next neighbour site. All possible
858 geometries of these pairs/trios were tested. For hydrogen atoms in $(2H)_{Mg}^X$, $(4H)_{Si}^X$, $(1H)'_{Mg}$,
859 $(3H)'_{Si}$ and $(2H)''_{Si}$ defects we considered them bound to an O in the vacancy. We calculated
860 the relative enthalpy of every possible arrangement of hydrogen in these vacancies where an
861 arrangement has each hydrogen bound to a specific O and pointing the hydrogen either in or
862 out of the vacancy. For H_{Int}^* the hydrogen was considered bound to an O1, O2 or O3 atom in
863 the bulk. The relative enthalpy of placing a defect in a specific site with a specific hydrogen
864 arrangement was then calculated as a function of pressure as shown in Table S1-S5. We also
865 calculated the enthalpy for all geometric arrangements (with each defect on a next neighbour
866 site with the enthalpies shown in Table S11-S13). For calculating the final free energy of the
867 reactions the most enthalpically stable defect for each arrangement was chosen and its free
868 energy calculated at high temperature. The effect of other arrangements is confined to the
869 configurational entropy term.

870 All possible configurations (with a defect in a specific site and hydrogen in a specific
871 arrangement) were then tabulated and their relative energy U_j assigned by applying energy
872 penalties determined from the relative enthalpies in Table S1-5. The energy penalty is
873 determined by the difference between the enthalpy of the defect in its current site with its
874 current hydrogen arrangement compared to the enthalpy of the defect in its favored site with
875 its favored hydrogen arrangement. This assumes that the energy of placing and moving a defect
876 around the crystal is independent of the other defects and that defect-defect interaction terms
877 are minimal.

878 To calculate the degeneracy (W) of each configuration, we must first calculate the
879 degeneracy at each site:

880
$$W = \ln \frac{N!}{a!b!\dots z!}$$
 Equation S5

881 Where N is the total number of sites, and a, b, c, \dots, z are the different types of
882 atoms/defects at each site including a final z term, which is simply $(N - a - b - \dots - y)$. To solve this
883 numerically, all defect concentrations were written in terms of defects/mol and then the Stirling
884 approximation was used ($\ln n! \cong n \ln n - n$), giving:

$$885 \quad W = N \ln N - N - a \ln a + a - b \ln b + b \dots - z \ln z + z \quad \text{Equation S6}$$

886 Additional degeneracies from hydrogen arrangement degeneracy and the degeneracy of the
887 bound pairs and trios were derived in a similar way added to this term.

888 Knowing the degeneracy and relative energy of all configurations, the entropy was
889 calculated using Equation S3 but summed across i , where i is simply a sum across every
890 configuration (j) appearing a number of times equal to its degeneracy (W).

891 In summary, each reaction proceeding to the right produces a set of defects, and then
892 these defects are spread across their different sites according to the energy differences between
893 these sites and the thermodynamic minimum of this distribution. This is determined by the state
894 of every other reaction. An alternative way to consider or calculate this is that (for example)
895 Reaction 5 is 4 reactions- one producing an M1 vacancy and an M1 interstitial, one producing
896 an M2 vacancy /M1 interstitial, one an M1 vacancy /I2 interstitial and one an I2 vacancy /M2
897 interstitial. However, this will produce the same answer as a single reaction producing a
898 vacancy and an interstitial that are then thermodynamically distributed across their two sites
899 including all the configurational entropy of the different distributions across the sites.

900

901 *1.2 Testing our assumptions*

902 For this model we assume that the relative energy of placing defects in different sites is
903 not a function of temperature, and that temperature effects occur only in differences between
904 different types of defect (such as V''_{Mg} and Mg''_I) and not between the same defects at different

905 sites (V''_{Mg} at M1 and M2 for example) as the different Mg sites are similar and thus their
906 vibrational frequencies should be similar.

907 This was tested for three defects Mg_I^{**} , V''_{Mg} and $(2H)''_{Mg}$. For the two Mg vacancies
908 (hydrous and anhydrous) it was found that the vibrational entropy difference between the two
909 sites was less than 0.1 eV/defect at 2000 K due to the large similarities between the two sites.
910 This is much lower than the enthalpy differences between these sites and this should be true
911 for most defects which do not have large differences in geometry between M1 and M2 sites.
912 Mg interstitials have very different geometries between M1 and I2 sites and their vibrational
913 entropies are also different. The vibrational entropy difference between these two sites is
914 tabulated in Muir et al. (Submitted) and included in the model and thus for Mg interstitials we
915 use G rather than U in Equation S3 and S4.

916 We also assume in this model that different arrangements of hydrogen have negligible
917 entropy differences. We tested this with two different arrangements in $(2H)''_{Mg}$ and $(4H)''_{Si}$.
918 For Mg we tested configurations 2 and 4 (based on their order in the Table S1) and found the
919 entropy difference was less than 0.085 eV/defect at 2000 K. For Si we tested configurations 1
920 and 3 (based on their order in Table S2) and found the entropy difference is less than 0.22
921 eV/defect at 2000 K- this is higher because these configurations are quite different where 4 has
922 a hydrogen outside the vacancy and 1 has all hydrogens inside. This is likely to be the largest
923 entropy difference of all the likely hydrogen arrangements due to the extreme difference in
924 geometry between these two arrangements. For $\{Ti_{Mg}(2H)''_{Si}\}$ we tested 4 different
925 arrangements (Row 13 Column 2, R2 C2, R1 C1 and R4 C14 in Table S3) and found
926 differences less than 0.103 eV/defect at 2000 K. These energies are still much lower than the
927 reaction energies and configurational entropy is only a small driver of these reactions so our
928 approximation of using U_j rather G_j is likely reasonably adequate. As shown in Table S7
929 when we rule out the formation of bound defect pairs we mostly assume that the bound pair

930 does not have a large increase in favourability with temperature and rely upon enthalpy to
931 determine if they are bound. This assumption was tested for some pairs as shown in Table S7
932 and was found to be the case.

933 We also assume that a quasi-harmonic approximation derived via linear displacement
934 at a single q-point is a good measure of the energy of these systems. In Muir et al. (2020) we
935 tested this assumption for dry vacancies and found it to be accurate. While hydrous vacancies
936 have considerable anharmonicities these largely cancel out as previously demonstrated from
937 ringwoodite and bridgmanite which have similar hydrous vacancies **REF**
938 **RINGWOODITEPAPER.**

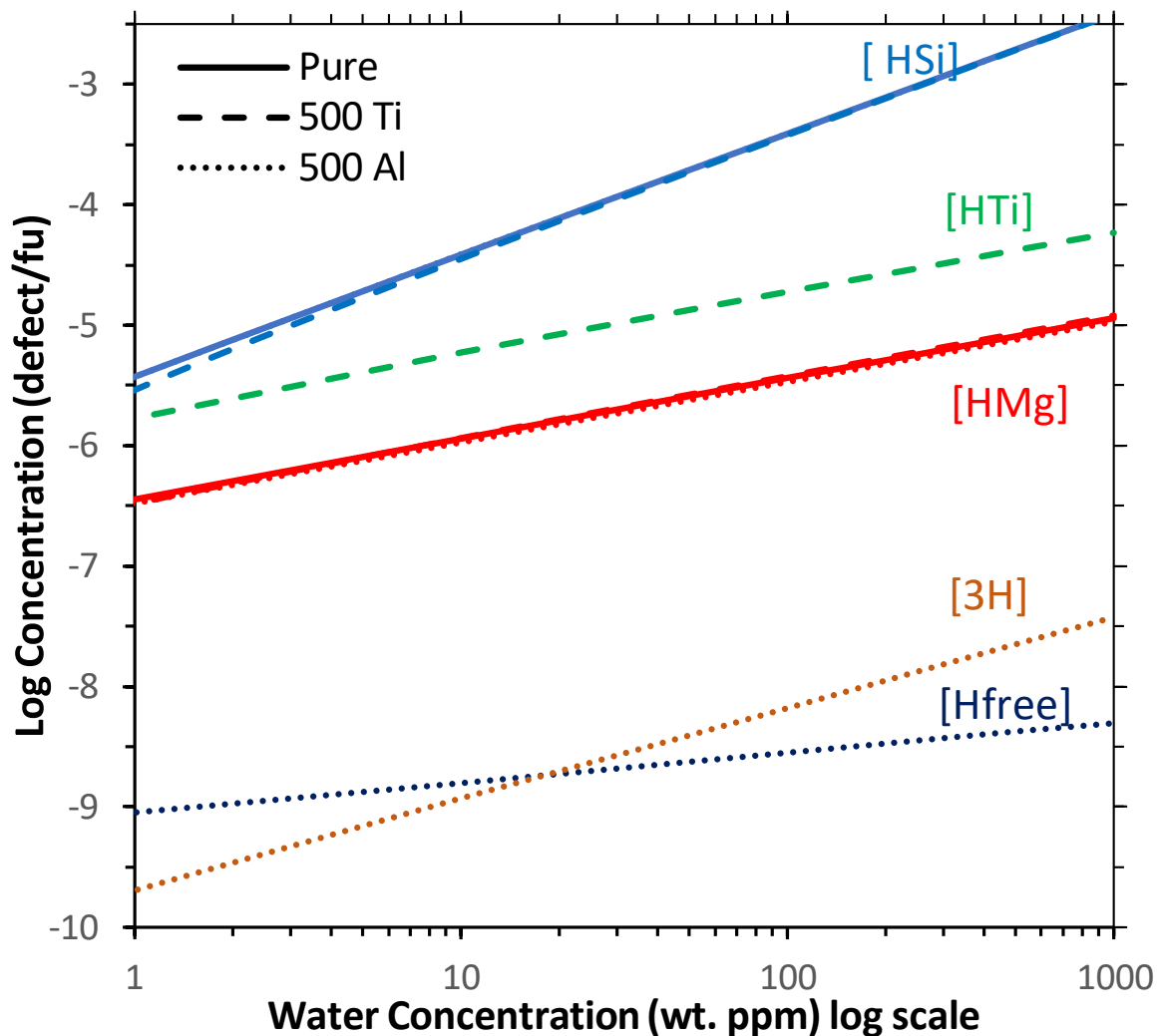
939

940 *1.3 Thermodynamic Minimisation*

941 Once we can determine the energy of any configuration, we need to find which
942 configuration of defects gives the lowest energy. This is a difficult problem as we are dealing
943 with variables that can have values that are many orders of magnitude different, multiple local
944 minimums and a configurational entropy term that has many terms and is difficult to solve
945 analytically. Instead we used a bespoke solver which minimised each variable in turn through
946 brute force and went through the variables multiple times. Such a method relies upon the large
947 energy differences of each of the different reactions (R1-R5). R1 is the most favoured reaction
948 and the progress of reactions R2-R5 has little effect on the progression of R1 because the energy
949 terms involved in R1 are much larger. Thus we solved each reaction in turn from most favoured
950 to least favoured and repeated this until the energy no longer varied. As stated in the text,
951 determining concentrations of defects that are below 1×10^{-20} defects/f.u. proved very difficult
952 as we encountered issues with floating points numbers and the precision of our calculations
953 (when the other defects had much higher concentrations) and thus we used this as a baseline
954 cutoff beyond which variables were not minimised. Our minimisation process does not present

955 a formal solution and may miss a true energy minimum and small variations in the final
 956 concentration of the products but should provide a good guide to how different conditions vary
 957 the concentration of the water products.

958

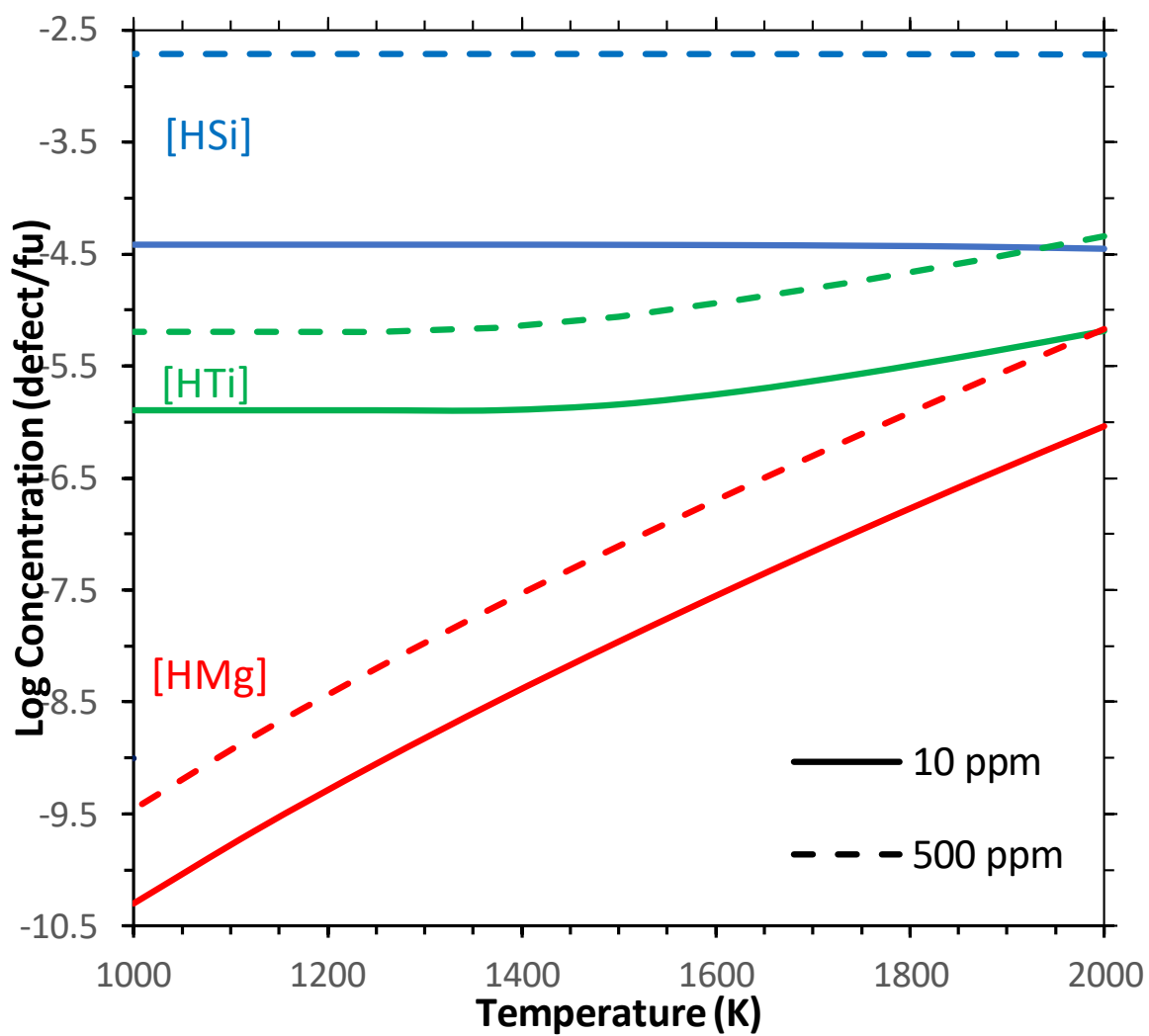


959

960 Figure S1 Distribution of products at 2000 K and 10 GPa (corrected) as a function of water
 961 content. Different colours represent different defects and lines different systems (solid line=
 962 pure forsterite, dashed line=forsterite+ 500 wt. ppm Al₂O₃, dotted line forsterite+500 wt. ppm
 963 TiO₂). Concentrations are defects/f.u. so [Si] has twice as much hydrogen as [Mg] with an
 964 equivalent concentration. [HSi] and [HMg] is near identical for all three compositions and
 965 cannot be distinguished at this scale. With increasing water [HSi] is favoured. [Hfree] is nearly
 966 identical with and without Ti and is around -14.25.

967

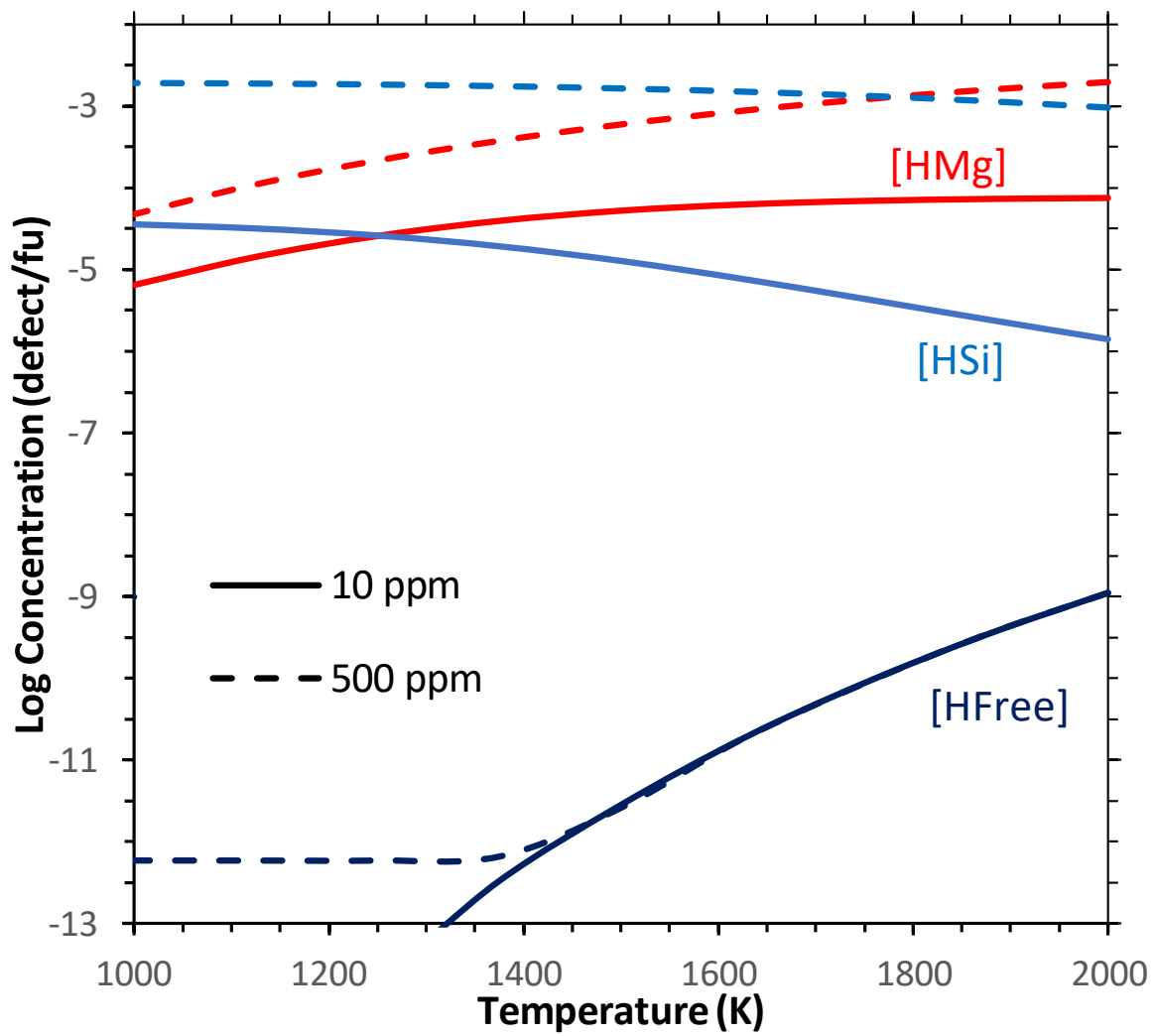
968



969

970 Figure S2: Distribution of the 3 major products as a function of temperature at 10 GPa
 971 (corrected) with 500 wt. ppm Al₂O₃ and TiO₂ with 2 different water contents (10 wt. ppm=
 972 solid lines, 500 wt. ppm dashed lines).

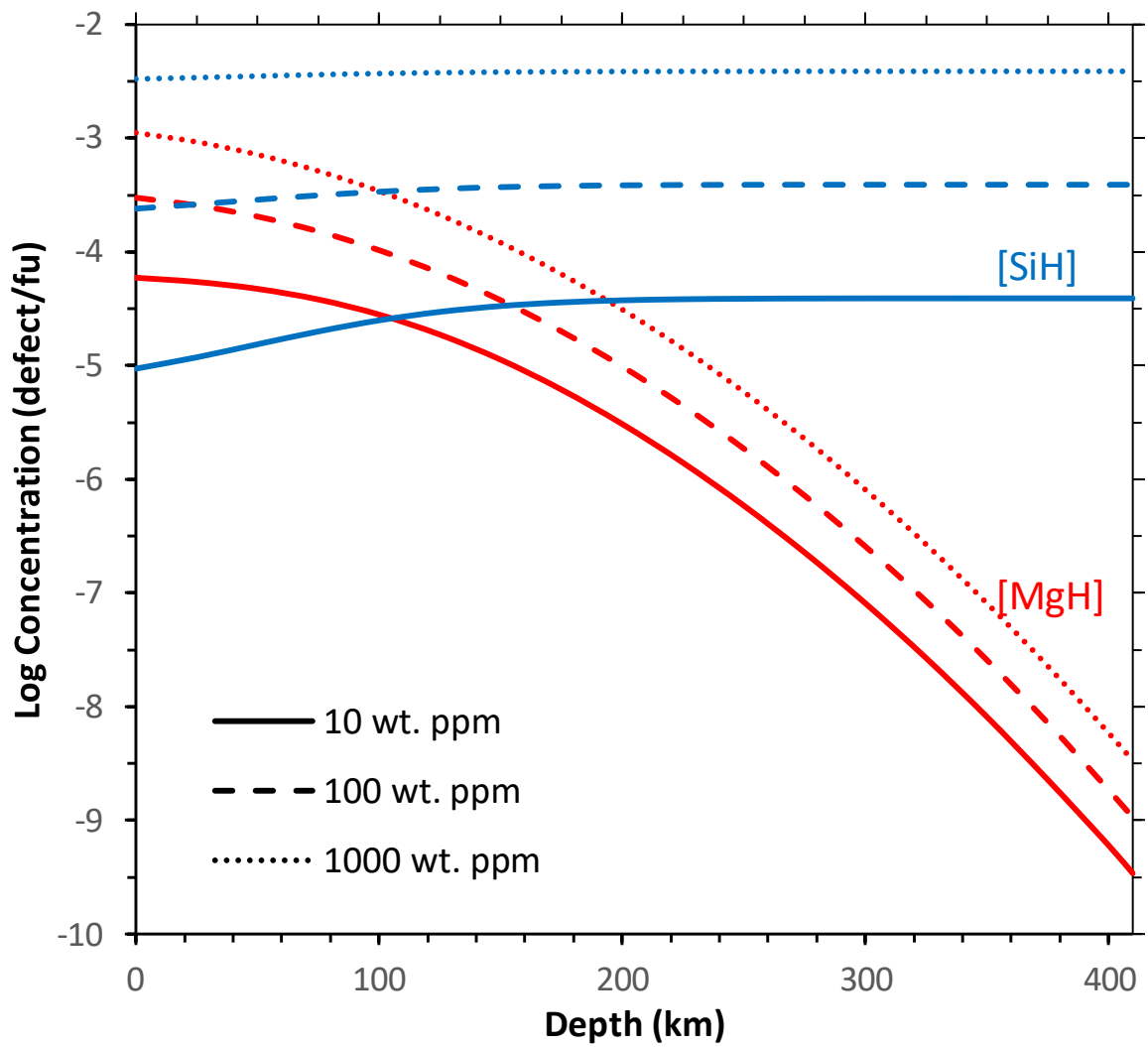
973



974

975 Figure S3: Distribution of the 3 major products as a function of temperature at 0 GPa (corrected)
 976 with pure forsterite and with 2 different water contents (10 wt. ppm= solid lines, 500 wt. ppm
 977 dashed lines).

978



979

980 Figure S4: Plot of the distribution of the three major products in pure forsterite along a geotherm
 981 with three different water concentrations (10 wt. ppm=solid lines, 100=dashed lines,
 982 1000=dotted lines).

983

984

| Arrangement | Degeneracy | Energy (eV) | | |
|-------------|------------|----------------------|-------|-------|
| | | 0 GPa (corrected) | 5 | 10 |
| O1i O1i | 1 | 0.501 | 0.503 | 0.489 |
| O1i O2i | 4 | 0.348 | 0.002 | 0.002 |
| O1i O3i | 4 | 0.536 | 0.561 | 0.575 |
| O2i O2i | 1 | 0.000 | 0.000 | 0.000 |
| O2i O3i | 4 | 0.544 | 0.525 | 0.503 |
| O3i O3i | 1 | 0.154 | 0.161 | 0.162 |
| O1i O1o | 2 | 1.265 | 1.370 | 1.456 |
| O1o O1o | 1 | 2.108 | 2.300 | 2.470 |
| O1o O2i | 4 | 1.174 | 1.269 | 1.352 |
| O1i O2o | 4 | 1.417 | 1.085 | 1.168 |
| O1o O2o | 4 | 2.374 | 2.585 | 2.835 |
| O1o O3i | 4 | 1.140 | 1.242 | 1.334 |
| O1i O3o | 4 | 0.944 | 1.048 | 1.138 |
| O1o O3o | 4 | 1.740 | 1.930 | 2.099 |
| O2i O2o | 2 | 0.982 | 1.085 | 1.170 |
| O2o O2o | 1 | 2.058 | 2.265 | 2.405 |
| O2o O3i | 4 | 1.480 | 1.586 | 1.612 |
| O2i O3o | 4 | 1.005 | 1.094 | 1.171 |
| O2o O3o | 4 | 2.297 | 2.515 | 2.635 |
| O3i O3o | 2 | 0.663 | 0.745 | 0.818 |
| O3o O3o | 1 | 1.276 | 1.435 | 1.582 |

985 Table S1: Relative enthalpy of different arrangements of hydrogen in $(2H)_{Mg}^x$ as a function of
986 pressure. Each arrangement is defined by the type of oxygen the hydrogen is bound to (O1,
987 O2, O3) and whether it points inside (i) or outside (o) the vacancy with the lowest enthalpy
988 possible for that arrangement listed in every case. Arrangements with hydrogen pointing
989 outside the vacancy are much higher in energy than those where all hydrogen point inside the
990 vacancy. These values are for $(2H)_{Mg}^x$ at the M1 site, values at the M2 site are similar but all
991 enthalpies at 0.51/0.59/0.59 eV higher at 0/5/10 GPa (corrected) respectively as $(2H)_{Mg}^x$ is
992 favoured at the M1. 0.51/0.59/0.59 eV is used for the site preference enthalpy of $(2H)_{Mg}^x$.

993

994

| Arrangement | Degeneracy | Energy (eV) | | |
|-----------------|------------|----------------------|-------|-------|
| | | 0 GPa (corrected) | 5 | 10 |
| O1i O2i O3i O3i | 1 | 0.494 | 0.606 | 0.554 |
| O1o O2i O3i O3i | 1 | 0.334 | 0.363 | 0.350 |
| O1i O2o O3i O3i | 1 | 0.000 | 0.000 | 0.000 |
| O1i O2iO3o O3i | 2 | 0.036 | 0.061 | 0.049 |
| O1o O2o O3i O3i | 1 | 0.350 | 0.412 | 0.385 |
| O1o O2i O3o O3i | 2 | 0.434 | 0.480 | 0.459 |
| O1i O2o O3o O3i | 2 | 0.136 | 0.213 | 0.175 |
| O1i O2i O3o O3o | 1 | 0.285 | 0.384 | 0.338 |
| O1o O2o O3o O3i | 2 | 2.200 | 0.465 | 0.269 |
| O1i O2o O3o O3o | 1 | 0.465 | 0.659 | 0.565 |
| O1o O2i O3o O3o | 1 | 1.914 | 2.227 | 2.076 |
| O1o O2o O3o O3o | 1 | 2.469 | 2.913 | 2.699 |

996 Table S2: Relative enthalpy of different arrangements of hydrogen in $(4H)_{Si}^x$ as a function of
997 pressure. Each arrangement is defined by the type of oxygen the hydrogen is bound to (O1,
998 O2, O3) and whether it points inside (i) or outside (o) the vacancy with the lowest enthalpy
999 possible for that arrangement listed in every case. The most stable arrangement has one
1000 hydrogen pointing outside the vacancy as also found by Qin et al. (2018).

| Arrangement | Degeneracy | 0 GPa (corrected) | | | | | | 5 GPa | | | | | | 10 GPa | | | | |
|-------------|------------|-------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|--------|-------|-------|-------|-------|
| | | M1 A | M1 B | M2 A | M2 B | M2 C | M2 D | M1 A | M1 B | M2 A | M2 B | M2 C | M2 D | M1 A | M1 B | M2 A | M2 B | M2 C |
| O3i O3i | 1 | 1.759 | 0.002 | 1.068 | 2.347 | 1.502 | 0.863 | 1.810 | 0.001 | 1.020 | 2.243 | 1.506 | 0.796 | 1.850 | 0.001 | 0.968 | 2.140 | 1.506 |
| O3i O2i | 2 | 1.960 | 1.228 | 0.995 | 1.038 | 1.688 | 1.085 | 2.009 | 0.000 | 0.923 | 0.253 | 1.683 | 1.041 | 2.046 | 0.003 | 0.857 | 0.201 | 1.683 |
| O3i O1i | 2 | 1.759 | 1.114 | 1.068 | 1.089 | 1.500 | 1.087 | 1.808 | 1.095 | 1.019 | 1.017 | 1.505 | 1.041 | 1.849 | 1.067 | 0.968 | 0.949 | 1.505 |
| O2i O1i | 1 | 1.961 | 1.236 | 1.229 | 0.316 | 3.252 | 3.291 | 2.009 | 1.239 | 1.191 | 0.264 | 3.265 | 3.292 | 2.046 | 1.239 | 1.145 | 0.216 | 3.265 |
| O3i O3o | 2 | 2.136 | 0.262 | 3.677 | 1.457 | 1.927 | 1.547 | 2.230 | 0.314 | 3.753 | 1.458 | 1.979 | 1.539 | 2.310 | 0.366 | 3.813 | 1.452 | 2.009 |
| O3o O3o | 1 | 2.756 | 2.641 | 4.694 | 4.753 | 2.584 | 2.591 | 2.915 | 2.799 | 4.862 | 4.872 | 2.706 | 2.686 | 3.060 | 2.942 | 5.006 | 4.977 | 2.804 |
| O3i O2o | 2 | 2.181 | 1.587 | 1.462 | 0.431 | 1.947 | 3.772 | 2.258 | 1.609 | 1.466 | 0.412 | 1.986 | 3.791 | 2.327 | 1.625 | 1.461 | 0.400 | 2.009 |
| O3o O2i | 2 | 2.249 | 0.261 | 3.783 | 1.813 | 2.041 | 1.454 | 2.351 | 0.314 | 3.855 | 1.772 | 2.091 | 1.480 | 2.437 | 0.364 | 3.905 | 1.453 | 2.140 |
| O3o O2o | 2 | 2.748 | 2.659 | 4.673 | 2.723 | 2.543 | 4.759 | 2.915 | 2.805 | 4.852 | 2.820 | 2.666 | 4.880 | 3.065 | 2.938 | 5.001 | 2.901 | 2.706 |
| O3i O1o | 2 | 6.759 | 5.002 | 6.068 | 5.316 | 5.665 | 5.863 | 6.810 | 5.001 | 6.020 | 5.264 | 5.854 | 5.796 | 6.850 | 5.001 | 5.968 | 5.216 | 6.020 |
| O3o O1i | 2 | 2.134 | 0.261 | 3.572 | 1.459 | 1.925 | 1.455 | 2.230 | 0.314 | 3.685 | 1.458 | 1.977 | 1.480 | 2.310 | 0.365 | 3.771 | 1.454 | 2.009 |
| O3o O2o | 2 | 2.133 | 0.261 | 3.572 | 1.457 | 6.239 | 3.920 | 2.229 | 0.313 | 3.687 | 1.458 | 6.503 | 4.123 | 2.310 | 0.364 | 3.780 | 1.451 | 6.759 |
| O2o O1i | 1 | 1.924 | 0.000 | 3.393 | 2.111 | 5.768 | 5.513 | 1.965 | 0.002 | 3.511 | 2.164 | 5.930 | 1.041 | 1.994 | 0.000 | 1.142 | 2.220 | 6.020 |
| O2i O1o | 1 | 2.249 | 1.432 | 1.466 | 0.431 | 3.389 | 3.736 | 2.340 | 1.472 | 1.466 | 0.412 | 1.990 | 3.808 | 2.416 | 1.503 | 1.463 | 0.400 | 2.009 |
| O2o O1o | 1 | 2.181 | 1.430 | 1.464 | 2.578 | 6.240 | 6.291 | 2.257 | 1.473 | 1.464 | 2.694 | 6.469 | 6.520 | 2.325 | 1.500 | 6.668 | 2.804 | 6.668 |

Table S3 Relative enthalpy of different arrangements of hydrogen in $\{Ti_{Mg}(2H)''_{Si}\}$ as a function of pressure. Each arrangement is defined by the type of oxygen the hydrogen is bound to (O1, O2, O3) and whether it points inside (i) or outside (o) the vacancy with the lowest enthalpy possible for that arrangement listed in every case. There are 6 Ti sites relative to the $(2H)''_{Mg}$ (see (Walker et al., 2007)), 2 in an M1 site which are each 2 fold degenerate and 4 in an M2 site which are each 1 fold degenerate.

| Arrangement | Degeneracy | Energy (eV) | | |
|-------------|------------|----------------------|-------|-------|
| | | 0 GPa (corrected) | 5 | 10 |
| O1i | 2 | 0.263 | 0.267 | 0.264 |
| O1o | 2 | 1.149 | 1.255 | 1.350 |
| O2i | 2 | 0.000 | 0.000 | 0.000 |
| O2o | 2 | 1.132 | 1.240 | 1.337 |
| O3i | 2 | 0.063 | 0.064 | 0.063 |
| O3o | 2 | 0.723 | 0.809 | 0.890 |

Table S4: Relative enthalpy of different arrangements of hydrogen in $(1H)'_{Mg}$ as a function of pressure. Each arrangement is defined by the type of oxygen the hydrogen is bound to (O1, O2, O3) and whether it points inside (i) or outside (o) the vacancy with the lowest enthalpy possible for that arrangement listed in every case. Arrangements with hydrogen pointing outside the vacancy are much higher in energy than those where all hydrogen point inside the vacancy.

| Arrangement | Degeneracy | Energy (eV) | | |
|-------------|------------|----------------------|-------|-------|
| | | 0 GPa (corrected) | 5 | 10 |
| O1i O3i O3i | 1 | 0.285 | 0.320 | 0.298 |
| O2i O3i O3i | 1 | 0.000 | 0.001 | 0.001 |
| O1i O2i O3i | 2 | 0.405 | 0.000 | 0.000 |
| O1i O3o O3i | 2 | 0.545 | 0.656 | 0.609 |
| O1o O3i O3i | 1 | 0.283 | 1.003 | 0.314 |
| O1o O3o O3i | 2 | 0.544 | 0.663 | 0.611 |
| O1i O3o O3o | 1 | 0.921 | 1.141 | 1.040 |
| O1o O3o O3o | 1 | 3.271 | 3.853 | 3.577 |
| O2i O3o O3i | 2 | 0.492 | 0.568 | 0.534 |
| O2o O3i O3i | 1 | 0.332 | 0.397 | 0.367 |
| O2o O3o O3i | 2 | 1.041 | 1.224 | 1.137 |
| O2i O3o O3o | 1 | 1.170 | 1.143 | 1.258 |
| O2o O3o O3o | 1 | 2.154 | 2.582 | 2.378 |
| O1i O2i O3o | 1 | 0.659 | 0.800 | 0.739 |
| O1i O2o O3i | 1 | 0.522 | 0.609 | 0.573 |
| O1o O2i O3i | 1 | 0.404 | 1.087 | 1.036 |
| O1i O2o O3o | 1 | 0.902 | 1.137 | 1.025 |
| O1o O2i O3o | 1 | 2.785 | 3.249 | 3.033 |
| O1o O2o O3i | 1 | 0.520 | 0.886 | 0.721 |
| O1o O2o O3o | 1 | 0.898 | 1.171 | 1.044 |

Table S5: Relative enthalpy of different arrangements of hydrogen in $(3H)'_{Si}$ as a function of pressure. Each arrangement is defined by the type of oxygen the hydrogen is bound to (O1, O2, O3) and whether it points inside (i) or outside (o) the vacancy with the lowest enthalpy possible for that arrangement listed in every case.

| | 0 GPa | | | 5 GPa | | | 10 GPa | | |
|-----|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| | 1000 K | 1500 K | 2000 K | 1000 K | 1500 K | 2000 K | 1000 K | 1500 K | 2000 K |
| R9 | -2.179 | -2.814 | -3.198 | -2.166 | -2.934 | -3.480 | -2.124 | -2.994 | -3.678 |
| R10 | -0.959 | -1.296 | -1.680 | -0.949 | -1.311 | -1.747 | -0.951 | -1.311 | -1.776 |
| R12 | 10.268 | 11.156 | 11.934 | 10.531 | 11.612 | 12.559 | 10.915 | 12.184 | 13.291 |
| R13 | 25.757 | 32.592 | 40.442 | 26.195 | 32.219 | 39.363 | 27.542 | 32.586 | 38.873 |
| R14 | 5.622 | 5.226 | 4.855 | 5.335 | 4.742 | 4.202 | 5.161 | 4.354 | 3.625 |
| R15 | 7.092 | 8.211 | 9.304 | 6.988 | 8.275 | 9.528 | 6.868 | 8.272 | 9.668 |
| R16 | 9.077 | 9.261 | 9.491 | 9.144 | 9.478 | 9.852 | 9.355 | 9.817 | 10.313 |
| R17 | 20.114 | 21.857 | 23.571 | 19.619 | 21.462 | 23.365 | 19.206 | 21.056 | 23.068 |
| R18 | 19.748 | 26.901 | 35.046 | 20.472 | 27.012 | 34.620 | 21.994 | 27.768 | 34.707 |
| R19 | 9.077 | 9.261 | 9.491 | 9.144 | 9.478 | 9.852 | 9.355 | 9.817 | 10.313 |
| R20 | 18.224 | 18.883 | 19.160 | 17.096 | 17.793 | 18.425 | 16.271 | 16.889 | 17.587 |
| R21 | 36.437 | 39.543 | 43.304 | 37.252 | 41.554 | 45.818 | 39.306 | 43.776 | 48.399 |

Table S6: Reaction energies (in eV/f.u) for minor reactions as a function of pressure and temperature.

| Temp | Pressure | [Al ₂ O ₃] wt. ppm | [H ₂ O] _{bulk} wt. ppm | | | | | | | |
|--------|----------|--|--|-------|-------|-------|-------|-------|-------|-------|
| | | | 1 | 5 | 10 | 25 | 50 | 100 | 250 | 500 |
| 2000 K | 5 | 10 | 1.349 | 1.005 | 1.017 | 1.074 | 1.201 | 1.509 | 2.665 | 5.213 |
| | | 25 | 1.240 | 1.002 | 1.007 | 1.030 | 1.082 | 1.205 | 1.628 | 2.410 |
| | | 50 | 1.161 | 1.001 | 1.004 | 1.016 | 1.042 | 1.105 | 1.317 | 1.684 |
| | | 100 | 1.101 | 1.001 | 1.002 | 1.008 | 1.022 | 1.055 | 1.165 | 1.351 |
| | | 250 | 1.052 | 1.000 | 1.001 | 1.004 | 1.010 | 1.024 | 1.073 | 1.155 |
| | | 500 | 1.031 | 1.000 | 1.000 | 1.002 | 1.006 | 1.014 | 1.042 | 1.088 |
| | 10 | 10 | 1.001 | 1.013 | 1.032 | 1.094 | 1.194 | 1.380 | 1.892 | 2.702 |
| | | 25 | 1.000 | 1.006 | 1.014 | 1.041 | 1.085 | 1.166 | 1.379 | 1.694 |
| | | 50 | 1.000 | 1.003 | 1.008 | 1.023 | 1.048 | 1.093 | 1.212 | 1.384 |
| | | 100 | 1.000 | 1.002 | 1.005 | 1.014 | 1.028 | 1.055 | 1.125 | 1.225 |
| | | 250 | 1.000 | 1.001 | 1.002 | 1.007 | 1.015 | 1.029 | 1.066 | 1.119 |
| | | 500 | 1.000 | 1.001 | 1.002 | 1.005 | 1.010 | 1.019 | 1.042 | 1.077 |
| | 15 | 10 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.001 | 1.002 | 1.005 |
| | | 25 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.001 | 1.001 | 1.003 |
| | | 50 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.001 | 1.002 |
| | | 100 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.001 | 1.001 |
| | | 250 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.001 |
| | | 500 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| 1500 K | 5 | 10 | 1.003 | 1.024 | 1.054 | 1.149 | 1.300 | 1.581 | 2.373 | 3.711 |
| | | 25 | 1.001 | 1.010 | 1.023 | 1.064 | 1.127 | 1.243 | 1.550 | 2.010 |
| | | 50 | 1.001 | 1.005 | 1.013 | 1.035 | 1.069 | 1.133 | 1.297 | 1.534 |
| | | 100 | 1.000 | 1.003 | 1.007 | 1.020 | 1.040 | 1.076 | 1.169 | 1.302 |
| | | 250 | 1.000 | 1.002 | 1.004 | 1.010 | 1.020 | 1.039 | 1.086 | 1.153 |
| | | 500 | 1.000 | 1.001 | 1.002 | 1.006 | 1.013 | 1.024 | 1.054 | 1.097 |
| | 10 | 10 | 1.001 | 1.004 | 1.007 | 1.014 | 1.023 | 1.040 | 1.079 | 1.134 |
| | | 25 | 1.001 | 1.002 | 1.004 | 1.007 | 1.012 | 1.021 | 1.042 | 1.071 |
| | | 50 | 1.000 | 1.001 | 1.002 | 1.005 | 1.008 | 1.014 | 1.027 | 1.046 |
| | | 100 | 1.000 | 1.001 | 1.002 | 1.003 | 1.005 | 1.009 | 1.018 | 1.030 |
| | | 250 | 1.000 | 1.001 | 1.001 | 1.002 | 1.003 | 1.005 | 1.011 | 1.018 |
| | | 500 | 1.000 | 1.000 | 1.001 | 1.001 | 1.002 | 1.004 | 1.007 | 1.012 |
| | 15 | 10 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| | | 25 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| | | 50 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| | | 100 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| | | 250 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| | | 500 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| 1000 K | 5 | 10 | 1.000 | 1.000 | 1.001 | 1.002 | 1.005 | 1.008 | 1.013 | 1.016 |
| | | 25 | 1.000 | 1.000 | 1.001 | 1.001 | 1.003 | 1.005 | 1.008 | 1.011 |

| | | | | | | | | | | |
|--|----|-----|-------|-------|-------|-------|-------|-------|-------|-------|
| | | 50 | 1.000 | 1.000 | 1.001 | 1.001 | 1.002 | 1.003 | 1.006 | 1.191 |
| | | 100 | 1.002 | 1.006 | 1.010 | 1.020 | 1.034 | 1.057 | 1.113 | 1.104 |
| | | 250 | 1.001 | 1.003 | 1.005 | 1.011 | 1.018 | 1.031 | 1.061 | 1.045 |
| | | 500 | 1.001 | 1.002 | 1.004 | 1.007 | 1.012 | 1.020 | 1.027 | 1.027 |
| | 10 | 10 | 1.000 | 1.000 | 1.001 | 1.002 | 1.003 | 1.004 | 1.008 | 1.014 |
| | | 25 | 1.000 | 1.000 | 1.000 | 1.001 | 1.002 | 1.003 | 1.005 | 1.009 |
| | | 50 | 1.000 | 1.000 | 1.000 | 1.001 | 1.001 | 1.002 | 1.004 | 1.006 |
| | | 100 | 1.000 | 1.000 | 1.000 | 1.001 | 1.001 | 1.001 | 1.003 | 1.004 |
| | | 250 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.001 | 1.002 | 1.003 |
| | | 500 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.001 | 1.001 | 1.002 |
| | 15 | 10 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| | | 25 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| | | 50 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| | | 100 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| | | 250 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| | | 500 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |

Table S7: (Al_{Mg}/Al'_{Si}) as a function of Al content, pressure, temperature and water content. For most conditions these are identical ($Al_{Mg} = Al'_{Si}$) which is the base state but at high temperatures, low pressures and low Aluminium large amounts of water changes this ratio significantly and in near linear fashion. In these conditions water concentration has a near linear effect on the ratio and thus measuring the ratio can tell you the water content.

| Temp | Pressure | [TiO ₂] wt. ppm | [H ₂ O] _{bulk} wt. ppm | | | | | | | |
|--------|----------|--------------------------------|--|-------|-------|--------|--------|--------|--------|--------|
| | | | 1 | 5 | 10 | 25 | 50 | 100 | 250 | 500 |
| 2000 K | 5 | 10 | 1.882 | 1.189 | 0.894 | 0.514 | 0.240 | -0.018 | -0.328 | -0.541 |
| | | 25 | 1.901 | 1.206 | 0.910 | 0.527 | 0.250 | -0.012 | -0.325 | -0.539 |
| | | 50 | 1.930 | 1.234 | 0.936 | 0.548 | 0.265 | -0.001 | -0.320 | -0.536 |
| | | 100 | 1.983 | 1.285 | 0.984 | 0.589 | 0.297 | 0.020 | -0.310 | -0.531 |
| | | 250 | 2.113 | 1.411 | 1.106 | 0.698 | 0.388 | 0.084 | -0.279 | -0.515 |
| | | 500 | 2.269 | 1.566 | 1.259 | 0.846 | 0.523 | 0.192 | -0.223 | -0.486 |
| | 10 | 10 | 1.577 | 0.935 | 0.684 | 0.384 | 0.179 | -0.012 | -0.248 | -0.418 |
| | | 25 | 1.612 | 0.961 | 0.704 | 0.397 | 0.186 | -0.007 | -0.245 | -0.416 |
| | | 50 | 1.665 | 1.002 | 0.737 | 0.417 | 0.199 | 0.000 | -0.242 | -0.414 |
| | | 100 | 1.757 | 1.078 | 0.799 | 0.458 | 0.226 | 0.016 | -0.234 | -0.410 |
| | | 250 | 1.956 | 1.259 | 0.961 | 0.578 | 0.308 | 0.065 | -0.212 | -0.398 |
| | | 500 | 2.165 | 1.462 | 1.157 | 0.749 | 0.443 | 0.154 | -0.171 | -0.377 |
| | 15 | 10 | 2.625 | 2.271 | 2.119 | 1.919 | 1.768 | 1.616 | 1.416 | 1.264 |
| | | 25 | 2.628 | 2.272 | 2.120 | 1.919 | 1.768 | 1.617 | 1.416 | 1.264 |
| | | 50 | 2.631 | 2.273 | 2.121 | 1.920 | 1.768 | 1.617 | 1.417 | 1.264 |
| | | 100 | 2.637 | 2.276 | 2.122 | 1.921 | 1.769 | 1.617 | 1.417 | 1.264 |
| | | 250 | 2.654 | 2.283 | 2.128 | 1.924 | 1.771 | 1.619 | 1.418 | 1.265 |
| | | 500 | 2.683 | 2.296 | 2.137 | 1.929 | 1.775 | 1.621 | 1.419 | 1.266 |
| 1500 K | 5 | 10 | 0.987 | 0.325 | 0.068 | -0.236 | -0.440 | -0.628 | -0.861 | -1.029 |
| | | 25 | 1.107 | 0.408 | 0.124 | -0.209 | -0.426 | -0.621 | -0.858 | -1.027 |
| | | 50 | 1.259 | 0.534 | 0.219 | -0.160 | -0.401 | -0.609 | -0.853 | -1.025 |
| | | 100 | 1.466 | 0.732 | 0.396 | -0.054 | -0.346 | -0.582 | -0.843 | -1.020 |
| | | 250 | 1.798 | 1.076 | 0.746 | 0.263 | -0.142 | -0.487 | -0.809 | -1.004 |
| | | 500 | 2.076 | 1.364 | 1.045 | 0.594 | 0.196 | -0.271 | -0.744 | -0.975 |
| | 10 | 10 | 1.240 | 0.851 | 0.691 | 0.483 | 0.329 | 0.280 | 0.025 | -0.151 |
| | | 25 | 1.287 | 0.870 | 0.704 | 0.491 | 0.333 | -0.028 | -0.182 | -0.336 |
| | | 50 | 1.362 | 0.903 | 0.726 | 0.504 | 0.177 | -0.027 | -0.181 | -0.335 |
| | | 100 | 1.498 | 0.969 | 0.771 | 0.529 | 0.182 | -0.024 | -0.179 | -0.335 |
| | | 250 | 1.790 | 1.151 | 0.903 | 0.609 | 0.192 | -0.019 | -0.176 | -0.333 |
| | | 500 | 2.066 | 1.380 | 1.095 | 0.741 | 0.224 | -0.003 | -0.167 | -0.328 |
| | 15 | 10 | 3.389 | 3.039 | 2.891 | 2.691 | 2.542 | 2.390 | 2.191 | 2.039 |
| | | 25 | 3.393 | 3.043 | 2.893 | 2.694 | 2.543 | 2.391 | 2.192 | 2.040 |
| | | 50 | 3.394 | 3.043 | 2.894 | 2.694 | 2.543 | 2.392 | 2.192 | 2.040 |
| | | 100 | 3.395 | 3.044 | 2.894 | 2.694 | 2.543 | 2.392 | 2.192 | 2.040 |
| | | 250 | 3.398 | 3.045 | 2.895 | 2.695 | 2.543 | 2.392 | 2.192 | 2.039 |

| | | | | | | | | | | |
|--------|----|-----|-------|-------|-------|-------|-------|--------|--------|--------|
| | | 500 | 3.403 | 3.049 | 2.896 | 2.695 | 2.543 | 2.392 | 2.192 | 2.039 |
| 1000 K | 5 | 10 | 1.882 | 1.189 | 0.894 | 0.514 | 0.240 | -0.018 | -0.328 | -0.541 |
| | | 25 | 1.901 | 1.206 | 0.910 | 0.527 | 0.250 | -0.012 | -0.325 | -0.539 |
| | | 50 | 1.930 | 1.234 | 0.936 | 0.548 | 0.265 | -0.001 | -0.320 | -0.536 |
| | | 100 | 1.983 | 1.285 | 0.984 | 0.589 | 0.297 | 0.020 | -0.310 | -0.531 |
| | | 250 | 2.113 | 1.411 | 1.106 | 0.698 | 0.388 | 0.084 | -0.279 | -0.515 |
| | | 500 | 2.269 | 1.566 | 1.259 | 0.846 | 0.523 | 0.192 | -0.223 | -0.486 |
| | 10 | 10 | 1.577 | 0.935 | 0.684 | 0.384 | 0.179 | -0.012 | -0.248 | -0.418 |
| | | 25 | 1.612 | 0.961 | 0.704 | 0.397 | 0.186 | -0.007 | -0.245 | -0.416 |
| | | 50 | 1.665 | 1.002 | 0.737 | 0.417 | 0.199 | 0.000 | -0.242 | -0.414 |
| | | 100 | 1.757 | 1.078 | 0.799 | 0.458 | 0.226 | 0.016 | -0.234 | -0.410 |
| | | 250 | 1.956 | 1.259 | 0.961 | 0.578 | 0.308 | 0.065 | -0.212 | -0.398 |
| | | 500 | 2.165 | 1.462 | 1.157 | 0.749 | 0.443 | 0.154 | -0.171 | -0.377 |
| | 15 | 10 | 2.625 | 2.271 | 2.119 | 1.919 | 1.768 | 1.616 | 1.416 | 1.264 |
| | | 25 | 2.628 | 2.272 | 2.120 | 1.919 | 1.768 | 1.617 | 1.416 | 1.264 |
| | | 50 | 2.631 | 2.273 | 2.121 | 1.920 | 1.768 | 1.617 | 1.417 | 1.264 |
| | | 100 | 2.637 | 2.276 | 2.122 | 1.921 | 1.769 | 1.617 | 1.417 | 1.264 |
| | | 250 | 2.654 | 2.283 | 2.128 | 1.924 | 1.771 | 1.619 | 1.418 | 1.265 |
| | | 500 | 2.683 | 2.296 | 2.137 | 1.929 | 1.775 | 1.621 | 1.419 | 1.266 |

Table S8: Log of (Ti_{Si}^X/Ti_{Mg}^{2H}) as a function of Ti content, pressure, temperature and water content. Adding water decreases this ratio by making more $\{Ti_{Mg}^{2H}\}_{Si}$, adding more Ti or increasing the temperature increases this ratio, changing the pressure has varied effect depending upon temperature. The effect of water on the value is nearly linear within a set P, T and Ti concentration for all conditions and thus measuring this ratio is a good measurement of water concentration.

| | Static | | | 1500 K | | | Key Concentration (0 GPa 1500 K) | Conclusion |
|--|--------|-------|-------|--------------|--------------|--------------|----------------------------------|------------|
| | 0 GPa | 5 | 10 | 0 | 5 | 10 | | |
| $Al_{Mg}^{\bullet} + (1H)_{Mg}'$ | -0.68 | -0.82 | -0.83 | not examined | not examined | not examined | 7200.548 | Unbound |
| $Al_{Si}' + H_{Int}$ | -2.26 | -2.48 | -2.55 | -1.68 | -2.00 | -2.11 | 1127.549 | Unbound |
| $Al_{Mg}^{\bullet} + (3H)_{Si}'$ | -0.93 | -0.95 | -0.95 | not examined | not examined | not examined | 3020.346 | Unbound |
| $Ti_{Mg}^{\bullet\bullet} + (2H)_{Si}''$ | -5.00 | -5.69 | -5.74 | not examined | not examined | not examined | <0.01 | Bound |

Table S9: Binding energy of some defect pairs. $Al_{Mg}^{\bullet} + Al_{Si}'$ is R10 (Table S6) and $2 * Al_{Mg}^{\bullet} + V_{Mg}''$ is R9 (Table S6). In each case we present the energy and then a key concentration which is the concentration at which the preference goes from unbound to bound pairs in a simplified system in which only these defects exist and they behave perfectly.

| Depth (km) | Temp (K) | Pressure (GPa) | Ti+Al concentration (oxide wt. ppm) |
|------------|----------|----------------|-------------------------------------|
| 0 | 1575.00 | 0.00 | 488.27 |
| 25 | 1586.28 | 0.83 | 370.43 |
| 50 | 1597.56 | 1.67 | 282.35 |
| 75 | 1608.84 | 2.50 | 216.21 |
| 100 | 1620.12 | 3.34 | 166.30 |
| 125 | 1631.40 | 4.17 | 128.47 |
| 150 | 1642.68 | 5.01 | 99.67 |
| 175 | 1653.96 | 5.84 | 77.65 |
| 200 | 1665.24 | 6.68 | 60.74 |
| 225 | 1676.52 | 7.51 | 47.70 |
| 250 | 1687.80 | 8.35 | 37.60 |
| 275 | 1699.09 | 9.18 | 29.75 |
| 300 | 1710.37 | 10.01 | 23.63 |
| 325 | 1721.65 | 10.85 | 18.83 |
| 350 | 1732.93 | 11.68 | 15.07 |
| 375 | 1744.21 | 12.52 | 12.09 |
| 400 | 1755.49 | 13.35 | 9.74 |
| 410 | 1760.00 | 13.69 | 8.94 |

Table S10: Details of our geotherm and the concentration of products along it. These points were achieved by extrapolation from Ono (2008) whereas those of Al concentration were from solving equation 13 in De Hoog et al. (2010) adjusted for Al_2O_3 weight. TiO_2 was set to the same as Al_2O_3 weight. All runs along a geotherm used these points, for some runs additional points were necessary for smoothing and these were determined by interpolating between the 3 nearest points.

| Arrangement | Degeneracy | Energy (eV) | | |
|-------------|------------|----------------------|-------|-------|
| | | 0 GPa (corrected) | 5 | 10 |
| M1a-Si | 1 | 0.315 | 0.323 | 0.329 |
| M1b-Si | 1 | 0.001 | 0.000 | 0.000 |
| M1c-Si | 1 | 0.000 | 0.000 | 0.000 |
| M1d-Si | 1 | 0.315 | 0.323 | 0.329 |
| M2a-Si | 1 | 0.128 | 0.063 | 0.006 |
| M2b-Si | 1 | 0.356 | 0.305 | 0.259 |
| M2c-Si | 1 | 0.340 | 0.294 | 0.255 |
| M2d-Si | 1 | 0.331 | 0.284 | 0.242 |

Table S11: Relative enthalpy of different arrangements of $\{Al_{Mg}Al'_{Si}\}$. In each case the Al_{Mg} was on a nearest neighbour or a next nearest.

| Arrangement | Degeneracy | 0 GPa (corrected) | Arrangement | Degeneracy | 0 GPa (corrected) |
|-------------|------------|----------------------|-------------|------------|----------------------|
| M1-M1-M1 | 1 | 0.941 | M2-M2-M2 | 1 | 2.249 |
| M1-M1-M1 | 1 | 0.085 | M2-M2-M2 | 4 | 2.181 |
| M1-M1-M1 | 4 | 1.356 | M2-M2-M2 | 4 | 1.946 |
| M1-M1-M1 | 4 | 1.008 | M2-M2-M2 | 4 | 1.966 |
| M1-M1-M1 | 4 | 0.736 | M2-M2-M2 | 4 | 1.931 |
| M1-M1-M1 | 4 | 0.614 | M2-M2-M2 | 4 | 2.276 |
| M1-M1-M1 | 4 | 0.634 | M2-M2-M2 | 4 | 1.841 |
| M1-M1-M1 | 4 | 1.128 | M2-M2-M2 | 2 | 1.758 |
| M1-M1-M1 | 2 | 1.057 | M1-M2-M1 | 4 | 1.799 |
| M2-M1-M2 | 2 | 0.669 | M1-M2-M1 | 2 | 1.789 |
| M2-M1-M2 | 4 | 0.614 | M1-M2-M1 | 1 | 1.623 |
| M2-M1-M2 | 2 | 0.742 | M1-M2-M1 | 4 | 1.503 |
| M2-M1-M2 | 2 | 0.590 | M1-M2-M1 | 4 | 1.461 |
| M2-M1-M2 | 4 | 0.356 | M2-M2-M1 | 4 | 2.008 |
| M2-M1-M2 | 1 | 0.000 | M2-M2-M1 | 4 | 2.210 |
| M2-M1-M1 | 4 | 0.969 | M2-M2-M1 | 4 | 1.895 |
| M2-M1-M1 | 4 | 0.757 | M2-M2-M1 | 4 | 2.268 |
| M2-M1-M1 | 4 | 0.562 | M2-M2-M1 | 4 | 2.026 |
| M2-M1-M1 | 8 | 0.541 | M2-M2-M1 | 2 | 1.871 |
| M2-M1-M1 | 2 | 0.506 | M2-M2-M1 | 2 | 1.754 |
| M2-M1-M1 | 2 | 0.081 | M2-M2-M1 | 4 | 1.723 |
| M2-M1-M1 | 8 | 0.949 | M2-M2-M1 | 4 | 1.778 |
| M2-M1-M1 | 8 | 0.820 | M2-M2-M1 | 4 | 1.870 |
| M2-M1-M1 | 4 | 0.697 | M2-M2-M1 | 4 | 2.029 |
| M2-M1-M1 | 4 | 0.540 | M2-M2-M1 | 4 | 1.625 |
| M2-M2-M2 | 1 | 2.292 | M2-M2-M1 | 4 | 1.793 |

Table S12: Relative enthalpy of different arrangements of $\{Al_{Mg} - V_{Mg}'' - Al_{Mg}\}$. Only enthalpy at 0 GPa was considered but considering the high relative enthalpy of nearly all arrangements except for 3 it is unlikely pressure or temperature has an effect on the configurational entropy. In each case a Al_{Mg} was placed in an M1 or an M2 site, V_{Mg}'' was placed in a next-nearest site and then Al_{Mg} in a next nearest site to the V_{Mg}'' . The most stable arrangements have all three sites in a single line.

| | | 0 GPa | 5 | 10 |
|---------------------------------------|-----------|--------|--------|--------|
| $(2H)_{Mg}^x$ | M1 | 0.000 | 0.000 | 0.000 |
| | M2 | 0.626 | 0.687 | 0.729 |
| $(1H)'_{Mg}$ | M1 | 0.000 | 0.000 | 0.000 |
| | M2 | 0.848 | 0.909 | 0.951 |
| H_{int} | O1 | 0.000 | 0.000 | 0.000 |
| | O2 | 0.326 | 0.301 | 0.275 |
| | O3 | 0.326 | 0.299 | 0.275 |
| V''_{Mg} | M1 | 0.000 | 0.000 | 0.000 |
| | M2 | 1.117 | 1.199 | 1.250 |
| $Mg_i^{\bullet\bullet}$ | M1 | 0.000 | 0.000 | 0.000 |
| | I2 Static | -0.004 | -0.155 | -0.237 |
| | I2 1000 K | 0.315 | 0.209 | 0.192 |
| | I2 2000 K | 0.468 | 0.372 | 0.378 |
| | I2 1000 K | 0.623 | 0.524 | 0.543 |
| Al_{Mg}^{\bullet} | M1 | 0.000 | 0.000 | 0.000 |
| | M2 | 0.012 | -0.055 | -0.107 |
| $V_o^{\bullet\bullet}$ | O1 | 2.269 | 2.327 | 2.367 |
| | O2 | 0.806 | 0.731 | 0.655 |
| | O3 | 0.000 | 0.000 | 0.000 |
| O_i'' | I1 | 1.203 | 1.180 | 1.156 |
| | I2 | 0.015 | 0.016 | 0.016 |
| | T1 | 1.487 | 1.542 | 1.609 |
| | T2 | 0.000 | 0.000 | 0.000 |
| | T3 | 0.015 | 0.017 | 0.015 |
| | T4 | 0.741 | 0.889 | 1.027 |
| | T5 | 0.017 | 0.018 | 0.016 |
| $Si_i^{\bullet\bullet\bullet\bullet}$ | I1 | 4.130 | 4.122 | 4.114 |
| | I2 | 1.927 | 1.821 | 1.978 |
| | T1 | 0.279 | 0.000 | 0.000 |
| | T2 | 1.660 | 1.519 | 1.641 |
| | T3 | 0.000 | 0.149 | 0.530 |
| | T4 | 0.000 | 0.150 | 1.654 |
| | T5 | 3.010 | 3.246 | 3.482 |

Table S13 Relative Enthalpy of different defects in different crystallographic sites- for sites containing hydrogen this is in their most stable arrangement. For $Mg_i^{\bullet\bullet}$ temperature variation is also shown to relative to the M1 site which is always set to 0. For definition of the O and Si interstitial sites see Muir et al. (2020).

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