

REVISION 1

1

2 **Hydrogen diffusion in Ti-doped forsterite and the preservation of** 3 **metastable point defects**

4 Michael C. Jollands^{1,2*}, José Alberto Padrón-Navarta³, Jörg Hermann^{1,4*}, Hugh St.C.
5 O'Neill¹

6 ¹Research School of Earth Sciences, Australian National University, Canberra, ACT 0200, Australia

7 ²Institut des Sciences de la Terre, Bâtiment Géopolis, Université de Lausanne, 1015 Lausanne,
8 Switzerland

9 ³Géosciences Montpellier, CNRS & Univ. Montpellier, 34095 Montpellier, France

10 ⁴Institute of Geological Sciences, University of Bern, 3012 Bern, Switzerland

11 *present address

12 Correspondence: michael.jollands@unil.ch

13

14 **Keywords:** Diffusion; Point defects; Nominally Anhydrous Minerals; FTIR
15 spectroscopy

16

17 **Abstract**

18 The effect of trace concentrations of Ti on the rate and mechanism of hydrogen
19 diffusion in pure forsterite was investigated experimentally. Forsterite doped with
20 350-400 ppm Ti (predominantly octahedral Ti³⁺, minor tetrahedral Ti⁴⁺) was prepared
21 by diffusing Ti into pure synthetic forsterite at high temperature (1500 °C), very low
22 oxygen fugacity (~QFM-5) at atmospheric pressure. The Ti-doped forsterite was then
23 diffusively hydroxylated in a piston-cylinder apparatus at much lower temperatures
24 (650-1000 °C) and higher oxygen fugacities, at 1.5-2.5 GPa, with chemical activities
25 buffered by forsterite-enstatite or forsterite-periclase and partial pressure of H₂O equal
26 to total pressure. This produced hydrogen concentration-distance profiles of several

1

27 hundred micrometres in length. Diffusion of hydrogen through the Ti-doped forsterite,
28 even at very high fO_2 , does not lead to redox re-equilibration of the high $Ti^{3+}/\Sigma Ti$ ratio
29 set during the synthesis of the starting material at extremely reducing conditions – the
30 metastable point defects are partially preserved.

31 Three main hydroxylated point defects are observed – hydroxyl is associated with Ti^{4+}
32 (titano-clinohumite point defects), Ti^{3+} (and possibly other trivalent cations) and M-
33 site vacancies. Concentration-distance profiles represent an interplay between
34 diffusion and reaction (i.e. site rearrangement) to form the observed point defects. In
35 all experiments, the concentration-distance profiles of the hydroxylated Ti defects
36 coincide with the concentration-distance profiles of the M-site vacancy substitution,
37 with the same crystallographic anisotropy. This suggests that the macroscopic
38 movement of hydrogen through the crystal is due to one diffusion mechanism (the
39 diffusion of hydroxylated M-site vacancies). The net H diffusion coefficient
40 ($\log D(\Sigma H)$), between 650-1000 °C, is:

41

$$42 \quad \log D(\Sigma H) = \log D_0(\Sigma H) + \left(\frac{-223(\pm 8) \text{ kJmol}^{-1}}{2.3RT} \right)$$

43

44 Where the value of $\log D_0(\Sigma H)$ parallel to [100] and [001] directions are -3.0 ± 0.4 and
45 -2.2 ± 0.4 respectively; diffusion is therefore around one order of magnitude faster
46 along the c axis than along the a axis. The diffusion of hydrogen is slightly faster in
47 Ti-doped forsterite than in pure forsterite. There is no effect of chemical activity or
48 oxygen fugacity on the rate of diffusion. Hydrogen diffusion profiles represent a
49 complex interplay between the movement of H through the crystal lattice and point-
50 defect reactions to maintain charge balance.

51

52

53

Introduction

54 Since the discovery of hydroxyl (OH) stretching bands in olivine nearly half a century
55 ago (Beran, 1969), considerable effort has been expended in determining the
56 concentration and speciation of hydrogen in nominally anhydrous mantle phases.

57 Understanding this is a prerequisite for understanding the total water budget of the
58 Earth (e.g. Bell and Rossman, 1992; Bolfan-Casanova, 2005; Demouchy and Bolfan-
59 Casanova, 2016 Hirschmann et al., 2005; Smyth et al., 2006). Several studies have
60 attempted to quantify the amount of water in mantle olivine by measuring its
61 concentration in rapidly emplaced xenoliths and xenocrysts where the original mantle
62 water signature should be preserved (e.g. Bell et al., 2004; Grant et al., 2007;

63 Kitamura et al., 1987). However, the extent to which mantle olivine can maintain its
64 original water signature between being entrained in melt to being erupted/emplaced,
65 for example, is a function of the hydrogen diffusion mechanism and its rate, which is
66 still a matter of debate (e.g. Demouchy and Mackwell, 2003; 2006; Du Frane and
67 Tyburczy, 2012; Ferriss et al., 2015; Kohlstedt and Mackwell, 1998; Mackwell and
68 Kohlstedt, 1990; Padrón-Navarta et al., 2014, Thoraval and Demouchy, 2014).

69 Additionally, if the diffusion rate of hydrogen is known, and diffusive water loss is
70 observed in olivine xenocrysts, constraints can be placed on the duration of ascent and
71 emplacement (e.g. Demouchy et al., 2006; Denis et al., 2013; Peslier and Luhr, 2006;
72 Peslier et al., 2008, 2015; Peslier and Bizimis, 2015). The water content of olivine can
73 also be an indicator of the petrogenetic processes accompanying the entrainment of
74 their host xenoliths by ascending melts from the mantle (e.g. Tollan et al., 2015).

75 At least four main mechanisms of hydroxyl substitution in olivine have been
76 observed: OH may be associated with Si vacancies, M-site vacancies (vacancies in the
77 octahedral site), traces of trivalent cations, or with Ti^{4+} in a point defect resembling a
78 unit of the titano-clinohumite structure. The coupled hydrogen-titanium substitution
79 studied here may also be an important mechanism for transport of water into the upper
80 mantle (Hermann et al., 2007; Shen et al., 2014; Wirth et al., 2001) and storage of
81 water in olivine therein (Berry et al., 2005, 2007b; Walker et al., 2007).

82 The diffusion of hydrogen is likely to be even more complex; several different
83 diffusion mechanisms have been identified, each with different diffusion rates
84 (Demouchy and Mackwell, 2003, 2006; Du Frane et al, 2012; Ingrin and Blanchard,
85 2006; Kohlstedt and Mackwell, 1998; Mackwell and Kohlstedt, 1990; Padrón-Navarta
86 et al, 2014). In addition, the different point defects may interact with one another
87 inside the crystal (e.g. Padrón-Navarta et al, 2014), thus creating or annihilating
88 hydroxylated sites. Understanding these issues is necessary both for interpreting
89 hydrogen in natural olivine and designing future experiments.

90 In this study, we aim to determine if trace quantities (hundreds of parts per million) of
91 titanium affect the rate of H diffusion relative to pure forsterite. For this purpose, we
92 have prepared forsterite crystals with a given amount of Ti, and a point-defect
93 structure that is relatively well constrained and homogeneous based on the findings
94 from an extensive study of Ti diffusion in forsterite in anhydrous conditions (Jollands
95 et al., submitted).

96

97

Methods

98

99 Preparation and characterization of starting material

100
101 Pure synthetic forsterite (grown by the Czochralski method, as used by Jollands et al.,
102 2014; purity reported in Zhukova et al., 2014) was doped with 350-400 ppm Ti by
103 diffusing this element into the crystal until a near constant concentration was reached
104 throughout. Oriented slabs of approximately 1x3x12 mm were cut from a single
105 crystal of pure forsterite with the shortest axis corresponding to *c*, i.e. the largest face
106 of the slab was parallel to (001). This orientation was chosen because Ti diffuses
107 fastest along [001] (Spandler and O'Neill 2010; Jollands et al., submitted). A pre-
108 sintered powder of forsterite-karooite-geikielite ($\text{Mg}_2\text{SiO}_4\text{-MgTi}_2\text{O}_5\text{-MgTiO}_3$) was
109 mixed with polyethylene oxide glue and pasted onto the two (001) faces; this three-
110 phase mix was chosen as it gave the fastest Ti diffusion at 1500 °C without any partial
111 melting (Jollands et al., submitted). The crystal-powder couple was then annealed in a
112 gas mixing furnace at very low $f\text{O}_2$ (QFM -5.2; 97% CO - 3% CO₂) for ~6 weeks at
113 1500 °C to allow the Ti to homogenise through the crystal by diffusion on octahedral
114 sites. The powder partially sintered to the slab surface; this was removed by gentle
115 polishing. This also likely removed any areas of high Ti associated with Ti diffusion
116 on tetrahedral sites. The doping gave the crystal a slight bluish hue. The slab was then
117 cut into cubes of approximately 1x1x1 mm, with sides parallel to the slab edges such
118 that each cube was oriented with faces representing (001), (010) and (100).
119 One such cube was mounted in epoxy, ground down by around 300 µm to reveal the
120 crystal core, and analysed from rim to rim (whole crystal traverse) by laser ablation
121 ICP-MS using a slit-shaped 6x100 µm beam from a 193 nm Lambda Physik Complex
122 excimer laser coupled to an Agilent 7700 ICP-MS (as described in Jollands et al.
123 2014). In each time slice, ⁴⁷Ti was counted for 0.3 s, ⁵⁷Fe and ²⁷Al (likely
124 contaminants) for 0.05 s and ²⁹Si (internal standard) for 0.01 s. The pulse rate was 5

125 Hz, energy was maintained around 50 mJ (monitored by an internal energy meter via
126 a beam splitter at the point of exit from the laser source), NIST610 was used as
127 primary standard and data were processed using Iolite (Paton et al., 2011) against the
128 standard values of Jochum et al. (2011) (452 ± 10 ppm Ti) with no glass-olivine matrix
129 correction made.

130 Full homogenization (along [001]) had not occurred (Figure 1); the core (~350 ppm)
131 was slightly lower in Ti than the rim (400 ppm). In addition, the Al concentration
132 profile showed some heterogeneity; one side of the crystal had approximately double
133 the Al concentration than the other. The Al profile is comprised of two flat sections;
134 one side of the crystal has 7.7 ± 1.1 ppm and the other 13.9 ± 2.3 ppm. The reason for
135 this behaviour is unknown; it may be that the Czochralski growth method led to some
136 minor sector zoning in the original crystal. The small amount of Fe (10-50 ppm) is
137 likely from contamination in the gas-mixing furnace; this is expected to be all Fe^{2+} at
138 the very reducing conditions of the Ti doping step (Mallmann and O'Neill, 2010).

139 Early preliminary attempts to homogenize cubes (i.e. cut 1x1x1 mm cubes *before the*
140 *anneal*, immerse these in powder then anneal) were unsuccessful, the cubes were
141 generally cracked after the high T low $f\text{O}_2$ anneal, which precluded their use in
142 hydroxylation experiments.

143

144 **Diffusion experiments**

145

146 Previous experiments to determine the diffusion of hydrogen in minerals have been
147 hampered by the difficulty of recovering whole, uncracked crystals from the piston
148 cylinder or cold-seal vessels after diffusion anneals (e.g. Demouchy and Mackwell,
149 2003, 2006). The method used in this study, once refined, had a 100% success rate of

150 crystal recovery of a total of 8 experiments. Large (6.3 mm outer diameter) thick-
151 walled, cold-swage silver capsules were used; the capsule and snug-fitting lid were
152 precision-milled from a solid bar of high-purity silver (Figure 2). The capsule design
153 and specifications are presented in Hack and Mavrogenes (2006). Cubes of forsterite
154 were placed inside the capsules in a buffer of either forsterite+enstatite or
155 forsterite+periclase (sintered from reagent grade MgO and SiO₂ powders, pressed into
156 pellets, fired at 1400 °C in air and then reground). Where *f*O₂ buffers were used (e.g.
157 Re-ReO₂ or Ag-Ag₂O), these were packed into the capsule before the silica activity
158 buffer. For reference, Re-ReO₂ and Ag-Ag₂O are approximately NNO+2 and
159 NNO+14, respectively at 850 °C, 1.5 GPa (see Pownceby and O'Neill, 1994; Assal et
160 al 1997).

161 The capsules were filled to around 80-90% of their inside volume with the powder-
162 crystal mix, then distilled water was added using a syringe until free water was visible
163 on the top of the powder. Where too much water was added, the excess was removed
164 using the corner of a tissue. The remainder of the capsule was then filled with the
165 two-phase buffer powder. A lid was then placed inside the capsule, and pressed shut
166 using a custom swaging tool. Excess Ag (the capsule is slightly deformed through
167 swaging) was removed from the side of the capsule using a lathe to return it to a good
168 cylindrical shape.

169 The amount of water added was very approximately calculated to fill the capsule
170 (minus the volume of the crystal and powder) at peak anneal conditions using P-V-T
171 values from Zhang and Duan (2005). In order to recover a crystal without cracks from
172 shearing or torsion in the piston cylinder, it is important that the capsule should not
173 deform excessively at any stage of the P-T path of the run. The large excess of water
174 keeps the three-phase buffer material as a fairly loosely bound powder, which helps

175 removing the crystal from the capsule after the run without the necessity for any
176 mechanical abrasion. The use of large silver capsules allows some flexibility; slightly
177 too much water can be added without leakage, the excess being taken up by the
178 capsule swelling into a barrel shape rather than losing their water (Figure 2). This
179 represents a considerable improvement on previous designs using welded gold
180 capsules; the capacity of the silver to stop leakage or H diffusion-out is significantly
181 better (the walls are thicker), and, because no welding is necessary, more water can be
182 added.

183 The capsules were run in an end-loaded 5/8" (15.9 mm) Boyd-type piston-cylinder
184 apparatus using MgO-graphite-NaCl assemblies wrapped in low-friction Teflon foil.
185 About 0.2 GPa pressure was applied initially at room temperature, before
186 temperatures were ramped up at 100 °C/min, monitored continuously using a type B
187 thermocouple sheathed in mullite, with the bead placed in intimate contact with the
188 capsule by fitting into a pit drilled into the capsule lid. The pressure was increased
189 concordantly with the temperature, in order to approximately follow the water
190 isochore. The high thermal conductivity of silver coupled with the presence of a fluid
191 phase keep thermal gradients extremely low (5-10 °C at 850°C) along the length of
192 the capsule (Hack and Mavrogenes, 2006), despite being considerably longer (~12
193 mm) than average capsules used in high temperature experiments.

194 Runs were stopped by turning off the power, such that the temperature dropped to
195 <100 °C in around ten seconds, and the pressure was then slowly released, manually.
196 Following decompression at the end of the run, the capsules were retrieved and
197 pierced using a 1 mm drill bit to verify the presence of water. The top and bottom of
198 the capsule was removed using a lathe, and the open cylinder was then placed into an
199 ultrasonic bath to loosen the powder. Generally the buffer powder and crystal simply

200 fell out, but where it did not the powder was picked out using tweezers. The cube was
201 further cleaned ultrasonically, oriented using the characteristic Si-O overtones in its
202 FTIR spectrum, placed on a sticky tape on the (010) face, mounted in epoxy, and
203 polished on two sides to around 400-600 μm thickness (see Table 2 for thicknesses)
204 using a diamond-impregnated grinding wheel, followed by diamond paste on cloth
205 laps. No attempt was made to remove crystals from the epoxy after polishing.

206

207 **FTIR analysis**

208

209 With the exception of measurements to determine the polarisation of each point defect
210 (see below), all other analyses were conducted using unpolarised light.

211 The mounts holding the doubly polished crystals were placed onto an automated
212 mapping stage on a Bruker Hyperion IR microscope with a liquid nitrogen-cooled
213 MCT detector coupled to a Bruker Tensor IR spectrometer. The measurement
214 chamber was continuously purged with dry air. Measurements were generally
215 composed of 128 scans with an effective spectral resolution of 2 cm^{-1} .

216 Two different analytical routines were used. In 'profile' mode, the aperture was
217 closed into a $\sim 25 \times 200\text{ }\mu\text{m}$ slit and unpolarised analyses were taken every $5\text{ }\mu\text{m}$ along
218 a line from one side of the crystal to the other. This was advantageous in terms of the
219 high spatial resolution (although the true spatial resolution is a complex function of
220 the focal plane and analytical geometry and certainly poorer than $25\text{ }\mu\text{m}$) and
221 favourable signal to noise ratio, but made the implicit assumption that diffusion was
222 effectively one-dimensional along the length of the slit. This assumption might not be
223 satisfied in such experiments where the diffusant (hydrogen) moves into the crystal
224 from all sides, which would give diffusion profiles differing in shape from theoretical

225 expectations, and perhaps not reaching zero concentration in the middle of the crystal
226 due to interference from diffusion from the other sides.
227 Accordingly, some crystals were also examined in two dimensions with unpolarised
228 light, with a 50x50 μm square aperture that mapped the entire crystal with 25-30 μm
229 steps, such that all analyses were overlapping. Sub-samples of the map were then
230 extracted along lines where diffusion appeared one-dimensional; i.e. no interference
231 from the other sides. This method has poorer spatial resolution but gives greater
232 confidence that the profiles are one-dimensional. Asymmetrical diffusion profiles
233 (discussed later) could only be analysed using the profile mode; the spatial resolution
234 of the mapping mode was too poor to resolve the short diffusion profiles associated
235 with the asymmetry.
236 Spectra were corrected for atmospheric H_2O and CO_2 using Bruker OPUS software,
237 and the background subtracted using a concave rubberband correction with 64
238 baseline points and three iterations. Given that polishing induced some minor
239 topography in the sample (thicker in the centre, thinner at the edges), the spectra were
240 then normalized to 1 cm thick using the empirical relationship of Shen et al. (2014)
241 derived from the integrated area underneath the Si-O stretching band region (for
242 measurements using unpolarised light). The integrated area (A_{int}) of these overtones
243 between 1625-2150 cm^{-1} is related to thickness (T_{sample}) using $T_{\text{sample}} (\mu\text{m}) =$
244 $A_{\text{int}}/0.553$. Systematic biases may occur from this thickness correction, as the method
245 was developed using randomly oriented grains, but for relative changes in OH content
246 (i.e. diffusion profiles) this will have no effect. Analyses with epoxy contamination
247 (at the crystal edge) were removed; these were identified both by the failure of the
248 concave rubberband to fully remove background in the OH region (3100-3600 cm^{-1})
249 as well as the characteristic overtones of organic material. Such spectra were removed

250 from consideration. The ‘interface’ spectra therefore represent the average spectra in
251 the first 25 μm when analyzing in profile mode, or the first 50 μm in mapping mode
252 (the assumption is made that the midpoint of the first analysis is at 12.5 μm from the
253 edge in profiles and 25 μm in maps).

254

255 **Results**

256

257 **Infrared spectra**

258

259 Several unpolarised interface spectra were fitted to a series of ideal peaks (Figure 3),
260 assumed as Gaussian, using the freeware OpticalFit, developed by, and available
261 from, CSIRO Australia (MacRae and Wilson, 2008). All fitted peaks are considered
262 to correspond to real absorption peaks in the spectra, with the exception of the low,
263 broad peak at 3252 cm^{-1} ; this is added to compensate for inadequate baseline
264 subtraction in this region. The most prominent peak in interface spectra is always at
265 3351 cm^{-1} , with a shoulder formed by a peak at 3349 cm^{-1} and an associated low peak
266 at 3313 cm^{-1} . These peaks are attributed to OH groups associated with Ti^{3+} on the M
267 sites. The most likely substitution mechanism for this defect is a $\text{Ti}^{3+}\text{-H}^+$ pair
268 replacing two Mg^{2+} on the octahedral sites (e.g. Berry et al., 2007a), with
269 stoichiometry $(\text{Ti}^{3+}\text{H})\text{SiO}_4$. This defect is notated [Ti-triv], where [triv] indicates a
270 trivalent cation. The peaks were speculatively examined by Berry et al (2007a), who
271 determined that a single trivalent cation-hydrogen pair can give up to three hydroxyl
272 bands where the trivalent cation substitutes on both the M1 and M2 sites, due to the
273 geometry of shared edges between octahedra.

274 The possibility for an $\text{Al}^{3+}\text{-H}^+$ defect (i.e. [Al-triv]) is present (~ 10 ppm Al in the
275 crystal), but there is no indication of this in the spectra (Al^{3+} -associated OH has a
276 band at 3345 cm^{-1} (Berry et al., 2007a).
277 It is possible that an Fe^{3+} -associated OH defect is present (i.e. [Fe-triv]; peaks at 3350,
278 3331 and 3310 cm^{-1} according to Berry et al., 2007a) and responsible for the shoulder
279 peak at 3349 cm^{-1} . This is, however, unlikely, firstly because the Fe content in the
280 crystal is low ($\sim 10\text{-}50$ ppm in the majority of the crystal, up to 90 ppm in some parts)
281 and secondly because the very low $f\text{O}_2$ of the pre-anneal would favour nearly pure
282 Fe^{2+} and there is no apparent difference in spectra between crystals hydroxylated at
283 high and low $f\text{O}_2$.
284 The two prominent peaks at high wavenumbers (3571 and 3524 cm^{-1}) are attributed to
285 the Ti-clinohumite point defect ($\text{MgTi}^{4+}\text{H}_2\text{O}_4$), herein [TiCh-PD], where a Ti^{4+} ion
286 replaces a single Mg^{2+} , and charge balance is accomplished by replacement of Si^{4+}
287 with two H^+ (Balan et al., 2011; Berry et al., 2005; Walker et al., 2007).
288 The low, broad peak at 3164 cm^{-1} is attributed to fully hydroxylated M-site vacancies;
289 a single Mg^{2+} cation replaced by two H^+ often observed in similar studies (Balan et
290 al., 2011; Crepisson et al., 2014; Demouchy and Mackwell, 2003, 2006, Umemoto et
291 al., 2011). This defect will be notated [Mg].
292 After defining the three hydroxylated defect populations ([TiCh-PD], [Ti-triv], [Mg]),
293 the integrated areas underneath each set of peaks were directly determined by
294 measurement from the unpolarised baseline corrected spectra.
295 The contributions from small, unidentified peaks at 3428 , 3580 and 3553 cm^{-1} are not
296 considered in analysis of profiles.

297

298 **Determining water content**

299

300 In order to determine total integrated absorbance (i.e. the sum of polarised absorbance
301 along the three orthogonal principal directions of the indicatrix), the polarization of
302 each hydrous defect was determined by rotating the forsterite cube through 180° on
303 two orthogonal sections below a stationary E-W polarizer and taking a series of
304 infrared spectra. The start and end of the series for the section parallel to (010)
305 corresponded to the electric vector parallel to [100] (E//[100]), and with E//[001]
306 when the crystal was rotated 90°. This was then repeated with an orthogonal (100)
307 section, rotating the crystal such that E//[010] and E//[001]. Polar plots are presented
308 in Figure 4.

309 As has been observed before (although not always interpreted as such), the absorption
310 associated with [TiCh-PD] is strongly polarized with the maximum absorbance when
311 E//[100] (Kitamura et al., 1987; Koch-Muller et al., 2006; Miller et al., 1987; Padrón-
312 Navarta et al., 2014; Walker et al., 2007).

313 The orientation of the absorber associated with the [Mg] is perpendicular to that
314 associated with [TiCh-PD] observed in the (010) plane. The strongest absorbance of
315 [Mg] is observed when E//[001], in accordance with theoretical calculations (Balan et
316 al., 2011, Crepisson et al. 2014).

317 [Ti-triv] is resolved into two peaks with opposite polarization; the strongest peak
318 (3351 cm^{-1}) shows strongest absorbance when E//[100] and the weaker peak is
319 strongest when E//[001]. This is the first determination of polarization of this defect;
320 Ti^{3+} was not among the trivalent cations considered in the *ab-initio* modeling of M^{3+} -
321 H^+ substitutions by Zhang and Wright (2010).

322 Using the known polarization of the defects, defect-specific correction factors can be
323 determined to convert unpolarised absorbance measured in sections parallel to the

324 (010) face ($\Sigma\text{Abs}_{(010)}$) to total absorbance (i.e. the sum of polarised spectra measured
325 in three mutually perpendicular directions; ΣAbs). The correction factors for each
326 defect are:

327

$$\Sigma\text{Abs}_{[\text{Mg}]} = \text{Abs}_{[\text{Mg}](010)} \times 2.09 \quad (1)$$

328

$$\Sigma\text{Abs}_{[\text{TiCh-PD}]} = \text{Abs}_{[\text{TiCh-PD}](010)} \times 1.97 \quad (2)$$

329

$$\Sigma\text{Abs}_{[\text{Ti-triv}]} = \text{Abs}_{[\text{Ti-triv}](010)} \times 2.28 \quad (3)$$

330

331 Note that the correction factors for [Mg] and [TiCh-PD] are ~ 2 ; this is a function of
332 near zero absorbance parallel to [010].

333 Several calibrations exist to convert total integrated absorbance to a quantified
334 hydrogen content usually either as ppm H₂O by weight or atomic proportion of H
335 relative to Si, e.g. H/10⁶Si. Most of these calibrations are assumed to apply to all OH
336 in a given mineral, that is, they are “mineral-specific” (Bell et al., 2003; Withers et al.,
337 2012) but there is evidence that different substitution mechanisms require different
338 absorption coefficients (Kovács et al., 2010), or that there is a general relationship
339 between wavenumber and absorption coefficient (Skogby and Rossmann, 1991,
340 Libowitzky and Rossmann, 1997). In this study, we use the calibrations of Bell et al.
341 (2003), Kovács et al (2010), Withers et al (2012), plus the calibration of Bell et al.
342 (2003) with absorption coefficients modified based on the wavenumber of the
343 absorber using the relationship determined by Libowitzky and Rossmann (1997).
344 Absorption coefficients for the different defects observed in this study are presented
345 in Table 1, showing the potential for a considerable range of water contents to be

346 extracted from a single measurement. Because the determination of these absorption
347 coefficients is still a matter of debate, ‘water’ contents will be presented
348 predominantly as unpolarised integrated absorbance measured in the (010) plane (i.e.
349 values from equations 1-3 must be used to convert these values into total integrated
350 absorbance). The calculated water contents (at the crystal edge) using these
351 calibrations are given in Table 2 only. Importantly, the absorption coefficients do not
352 affect diffusion coefficients – diffusion in this system is independent of the
353 concentration of diffusing hydrogen, nor do they affect calculations based on *relative*
354 concentrations of the same defect in different experiments.

355

356 **Interface OH concentrations**

357

358 The concentrations of OH extrapolated to the crystal/fluid interface should be the
359 equilibrium concentrations towards which diffusion progresses. In these experiments
360 this interface concentration is not a global equilibrium but a metastable one (where
361 ‘interface’ refers to the closest measurement to the crystal edge within the spatial
362 resolution of FTIR in this configuration), determined by the initial state of the crystal
363 as imposed during its preparation at 1500 °C. It should be noted that our ‘metastable
364 equilibrium’ is not the same metastable equilibrium described in the classic work of
365 Kohlstedt and Mackwell (1998) and recently discussed by Ferriss et al (2015), but still
366 refers to the same type of situation – an apparent equilibrium that will be eliminated if
367 anneals are conducted at higher temperatures or for longer times. This is discussed
368 below in relation to the effect of oxygen fugacity on interface concentrations.

369 The total concentration of hydrous defects at the interface (i.e. the total integrated area
370 of peaks in the OH region) increases exponentially as a function of increasing

371 temperature (Tables 2-3, Figure 5b). The [Ti-triv] and [Mg] defects show similar
372 relationships (Figure 5a). The concentration of H associated with [TiCh-PD],
373 however, changes only a little as temperature increases, with considerable scatter.
374 The interface concentrations of all the defects increase with increasing pressure
375 (Table 2; Figure 5b). Decreasing αSiO_2 leads to lower OH concentration at the
376 interface, but the change is almost entirely taken up by [Ti-triv] (Figure 6; Tables 2-
377 3).

378

379 **Treatment of diffusion profiles**

380

381 The intensity of the bands in the OH stretching region all decrease from the rim to the
382 core of the crystals (e.g. Figure 7). As a preliminary treatment of the data, the
383 integrated area under all three peak populations was summed together; this gives a
384 simple indication of bulk diffusion rate without any consideration of defect specifics.
385 These data (integrated area measured using unpolarised light as a function of distance)
386 were then fitted to the solutions to Fick's second law for two boundary conditions.
387 Where traverses were conducted across the entire length of the crystal and diffusion
388 was symmetrical, concentration-distance profiles were fit to the solution for one-
389 dimensional, concentration independent diffusion from an infinite source into a finite
390 slab from Carslaw and Jaeger (1959); this is the same solution used by Demouchy and
391 Mackwell (2003) in similar experiments:

392

$$C(x) = (C_{\text{rim}} - C_{\text{core}}) \cdot \left(\operatorname{erfc} \frac{x}{2\sqrt{Dt}} + \operatorname{erfc} \frac{X-x}{2\sqrt{Dt}} \right) + C_{\text{core}} \quad (4)$$

393 Where the analytical traverse only covered a small portion of the crystal, i.e. where
394 the diffusion distances were very short or the diffusion was asymmetrical, the simple
395 equation for one-dimensional diffusion into a semi-infinite slab was used (e.g., Crank
396 1975):

397

$$C(x) = (C_{\text{rim}} - C_{\text{core}}) \cdot \text{erfc} \frac{x}{2\sqrt{Dt}} + C_{\text{core}} \quad (5)$$

398

399 In these equations, $C(x)$ is the concentration of the diffusant at position x , C_{rim} is the
400 equilibrium (interface) concentration, C_{core} is the background (initial) concentration,
401 erfc is the complimentary error function, X (in (4)) is the total length of the profile
402 (edge to edge of the crystal) in metres, D is the chemical diffusion coefficient (in m^2s^{-1})
403 and t is the duration of the experiment, in seconds. The C_{core} term is necessary given
404 that some profiles showed non-zero water contents in the core – probably related to a
405 contribution from diffusion along the third axis ([010], the b axis) of the cube.

406 In all experiments, the total integrated absorbance in the OH region (sum of all
407 defects) could be satisfactorily fitted to these equations. The results are presented in
408 Table 2 as $\log D(\Sigma H)$ for H diffusion along both the a and c axes (i.e. [100] and
409 [001]). The errors on $\log D$ were determined manually using the estimated maximum
410 and minimum values that allowed fits within the data scatter. Insofar as these
411 uncertainties correspond to approximately 95% confidence limits, they should be
412 approximately equivalent to two standard deviations.

413

414 **Defect specific diffusion**

415

416 With the exception of the ‘two-slope’ sides of asymmetrical profiles (discussed
417 below), the integrated areas corresponding to each of the three substitution types
418 could be individually fitted as a function of distance to equations (4) or (5). A map,
419 plus extracted, fitted profiles from all defects along both the *a* and *c* axes is shown in
420 Figure 8.

421 The results of curve-fitting are shown in Table 2. In all cases except perhaps
422 experiment hydrol4 (2.5 GPa, 850 °C), the apparent diffusion coefficients of H
423 associated with the three different defect substitution mechanisms overlap within
424 error. In the hydrol4 experiment, the [TiCh-PD] concentration-distance profile is
425 slightly longer than the profile associated with either [Ti-triv] or [Mg], but the
426 difference between error bar tips is equivalent to only 0.1 in $\log_{10}D$. Notably, the
427 anisotropy of H diffusion shown by the three defects is the same. In all cases,
428 diffusion is faster along [001] than along [100].

429

430 **Asymmetrical profiles**

431

432 All [001] profiles from 850 °C and 950 °C experiments show some asymmetry, with
433 one side showing higher [TiCh-PD] and lower [Ti-triv] concentrations than the other.
434 This behaviour is not observed in the 1000 °C experiment. Whether it is seen in the
435 650 °C and 750 °C experiments is not clear; the hydroxyl concentrations are too low
436 to resolve the behaviour of each defect.

437 In these profiles, the high [TiCh-PD]/low [Ti-triv] side shows concentration-distance
438 profiles that cannot be fitted to the theoretical equations (4) or (5). This side of the
439 profile is also associated with a low, sharp peak at 3428 cm^{-1} . An example of such a
440 profile is shown in Figure 9; the relative [Ti-triv]:[TiCh-PD] defect ratio is

441 considerably different from one side of the crystal to the other. In such profiles, the
442 side where all defects can be individually fitted to equation (5) is termed ‘simple’
443 and the side with higher [TiCh-PD] concentrations and mismatch to the theoretical
444 diffusion equations is termed ‘two-slope’ given the clear break of slope in the profile.
445 All further discussion of diffusion, except where explicitly referring to asymmetrical
446 profiles, will address the ‘simple’ sides of the profiles. These anomalies may be
447 related to non-stoichiometry caused by vapour loss, or perhaps some other
448 contamination, introduced during the preparation of the crystal, which involved long
449 annealing at very high temperatures. However, any detailed explanation would be
450 speculative. Suffice it to note that, all diffusion coefficients reported here are taken
451 from the other side of the crystals or determined from the sum of all defects (which
452 always displays an error function shape).

453

454 **H diffusion as a function of P, T, $a\text{SiO}_2$ and $f\text{O}_2$**

455

456 Neither $f\text{O}_2$ nor $a\text{SiO}_2$ have any influence on the rate of hydrogen diffusion, within
457 error (Table 2, Figure 6). In the MgO buffered experiment, there is no visible Si
458 vacancy substitution (i.e. $\text{Mg}_2\text{H}_4\text{O}_4$), within the spatial resolution of FTIR.
459 Although only two pressure conditions were investigated, the effect of pressure on the
460 diffusion of hydrogen is constrained to be small (Figure 10, Table 2), and given the
461 lack of outside-error difference in diffusion coefficients between the 1.5 GPa and 2.5
462 GPa experiments, it is not possible to determine any activation volume of diffusion.
463 Over the 350 °C temperature range investigated, $\log_{10}D$ (c , total) increases by over
464 three orders of magnitude (Figure 11). A similar change with temperature is seen for
465 diffusion along [100]. Following Demouchy and Mackwell (2003), a global fit (using

466 least squares) was performed for [100] and [001] diffusion coefficients (total
467 absorbance) to determine the activation energy (E_A) and pre-exponential factor D_0
468 using the relationship $D=D_0.\exp(E_A/RT)$ (i.e. $\log_{10}D = \log_{10}D_0+(E_A/2.3RT)$, where
469 2.3 is the natural logarithm of 10). We assume that E_A is the same in each direction.
470 The least-squares minimization gives a good fit to the data and yields the relationship:
471

$$\log D(\Sigma H) = \log D_0(\Sigma H) + \left(\frac{-223(\pm 8) \text{kJmol}^{-1}}{2.3RT} \right) \quad (6)$$

472
473 Where $D_0[100] = -3.04 \pm 0.4$ and $D_0[001] = -2.18 \pm 0.4$, i.e. diffusion along [001] is one
474 order of magnitude faster than along [100]. The fit is shown as solid black lines in
475 Figure 11.

476

477

478 Discussion

479

480 Previous determinations of mechanisms and rates of hydrogen diffusion

481

482 The addition of positive charge caused by protonation must be charge-balanced by
483 either diffusion-in of a negative species or diffusion-out of another positively charged
484 species. Here we use the term “species” to refer to a point-defect identity that may be
485 an ion either on a lattice site or interstitial, a vacancy in the lattice, or an electron or
486 electron hole (polaron).

487 Conceptually, it might seem reasonable that the fastest mechanism of H diffusion in
488 natural olivine is one in which involves the smallest, lightest species, i.e. where

489 charge-balance is achieved by reducing pre-existing Fe^{3+} to Fe^{2+} (Kohlstedt and
490 Mackwell, 1998; Mackwell and Kohlstedt, 1990). The reduction of Fe^{3+} can be
491 thought of as eliminating polarons (electron holes), thus this mechanism may be
492 described as proton-polaron exchange. This mechanism depends on the presence of
493 initial Fe^{3+} , whose concentration in natural olivine is only at the tens to hundreds of
494 ppm level (e.g. Dohmen and Chakraborty, 2007; Mallmann and O'Neill, 2009).
495 A slower mechanism (although still extremely fast when compared to Mg, Si and O
496 diffusion in olivine) uses M-site (octahedral, magnesium/iron site) vacancies for
497 charge balance (e.g. Demouchy and Mackwell, 2003; Demouchy and Mackwell,
498 2006). The coupled diffusion-in of a vacancy and two protons necessarily removes
499 Mg from the crystal, hence this mechanism should depend on chemical potentials; if
500 Mg is lost then the reaction should be favoured at low activity of magnesia (MgO).
501 Diffusion along this path is anisotropic; fastest along the c ([001]) crystallographic
502 axis, relating to the presence of tightly spaced M-site chains along this direction
503 (Demouchy and Mackwell, 2003).
504 The last mechanism that does not involve some coupled substitution with an alien
505 cation involves vacant tetrahedral sites (Si^{4+} sites) charge-balanced by four protons.
506 Diffusion along this pathway is likely to be close to isotropic; the tetrahedral sites are
507 relatively evenly spaced in different crystallographic directions. This mechanism
508 displaces silicon from the crystal, so is expected to have the opposite dependence on
509 chemical potentials as the M-site pathway. This was recently studied in terms of
510 hydrogen diffusion-out by Padrón-Navarta et al. (2014) and found to be orders of
511 magnitude slower than diffusion involving M-site vacancies.

512

513 **Defect formation and diffusion mechanisms – this study**

514

515 In this and the following sections, equilibria involving point defects will be presented
516 in Kröger-Vink notation, as has become conventional. In this notation, the main
517 letters represents the species (e.g., Mg = magnesium, Ti = titanium, V = vacancy),
518 subscript is the site location (Mg=octahedral [assume pure forsterite], Si=tetrahedral,
519 O=oxygen, i=interstitial) and superscript is charge excess or deficiency on the site
520 (^x=no charge excess/deficiency, [']=single charge deficiency, ^{*}=single charge excess). A
521 neutral charge exists when the tetrahedral site contains a 4+ cation, octahedral 2+,
522 oxygen 2- and interstitial 0. Following Walker et al (2007), coupled defects (i.e.
523 coupled for charge balance) are contained within curly braces. Herein, following
524 Ingrin and Blanchard (2006), a fully protonated M-site vacancy is notated
525 $\{V_{Mg}^{//} + 2H_i^*\}$, i.e. M-site vacancy charge-balances the protons on interstitial sites.
526 Without detailed structural knowledge, which might be obtainable by modeling (e.g.,
527 Balan et al, 2011, Walker et al. 2007, Crepisson et al. 2014), claiming specific site
528 occupancies for the H substitutions is dubious. For simplicity, the latter substitution
529 could also be written as $(2H)_{Mg}^x$, assuming that the two protons are directly on the M-
530 site (this is unlikely to be correct), or, probably most accurately, $\{V_{Mg}^{//} + 2OH_O^*\}$, with
531 the hydrogen associated with nearby oxygen. The actual positions of the H have no
532 effect on the stoichiometry of the point-defect reactions.
533 To understand the diffusion of H through Nominally Anhydrous Minerals, three types
534 of reactions must be considered. Firstly, there is the formation of defects at the crystal
535 edge, which represent the equilibrium situation and should give the equilibrium
536 concentrations of the defects at the conditions of T, P and chemical potentials
537 imposed in the experiments. In these reactions, free H₂O, MgO, O₂ etc are permissible
538 components. Using our analytical technique, we do not see the true interface, but the

539 near interface region, which is then extrapolated back to the crystal edge. The second
540 reaction type describes the movement of species through the crystal, which is
541 responsible for the macroscopic diffusion. The third type of reaction is akin to order-
542 disorder reactions in crystals, and describes the reaction between one kind of hydrous
543 defect with an anhydrous component to produce another kind of hydrous defect. As
544 such reactions involve transfer only on the unit-cell scale, usually they may be
545 expected to be fast relative to the macroscopic transport of material through crystals,
546 but this need not always be the case, and perhaps such exchange reactions could on
547 occasion be rate-limiting.

548 The crystal chemistry of the Ti in the starting material, which was synthesized at 1500
549 °C under anhydrous conditions, can be deduced from previous work. Hermann et al.
550 (2005) showed that the substitution of Ti^{4+} in olivine under anhydrous conditions and
551 in the absence of charge-balancing by aliovalent impurities such as Al^{3+} or B^{3+} occurs
552 as $\text{Mg}_2\text{Ti}^{4+}\text{O}_4$, with Ti^{4+} substituting for Si^{4+} on the tetrahedral site (see also Walker et
553 al. 2007).

554 Jollands et al. (submitted) postulated that the substitution of Ti in olivine in the
555 (anhydrous) experimental conditions used in the Ti-doping stage can be described by
556 $\text{Mg}_2\text{Ti}^{4+}\text{O}_4$ and $(\text{Ti}_{4/3}^{3+}[\text{vac}]_{2/3})\text{SiO}_4$, that is, Ti^{4+} on the T-sites and Ti^{3+} on the M sites
557 charge balanced by M-site vacancy ([vac]). This was inferred based on a relationship
558 between Ti diffusion and $f\text{O}_2$ (diffusivity as a function of $f\text{O}_2$ followed a sigmoidal
559 pattern consistent with a one electron transfer reaction), characteristic diffusion
560 profile shapes related to Ti^{4+} being ‘trapped’ on the T-sites (stepped diffusion profiles
561 at high $f\text{O}_2$, suggesting that the diffusing species [Ti^{4+}] has two possible site locations
562 with different diffusivities [T and M]) and FTIR analysis of hydroxylated diffusion
563 profiles. At the T- $f\text{O}_2$ conditions of Ti doping, the equilibrium amount of $\text{Ti}^{3+}/\Sigma\text{Ti}$ is

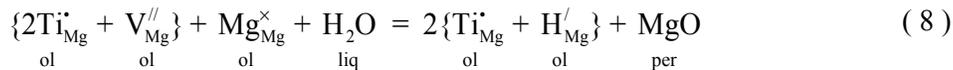
564 around half (Mallmann and O'Neill, 2010), and the Jollands et al. study (submitted)
565 suggests that Ti^{3+} is favoured over Ti^{4+} by the kinetic nature of doping by diffusion.
566 The FTIR spectra suggest that the three main OH substitutions are [TiCh-PD], [Ti-
567 triv], and [Mg]. [Ti-triv] and [Mg] are associated with an M-site vacancy, whereas
568 [TiCh-PD] involves a T-site vacancy. Nevertheless, the concentration-distance
569 profiles of the substitution mechanisms have the same length (estimated) in each
570 experiment, in each crystallographic orientation. At first glance, this might seem
571 surprising, as the rates of both major-element diffusion (e.g. Chakraborty, 1997;
572 Chakraborty et al., 1994; Dohmen et al., 2002) and hydrogen diffusion (Demouchy
573 and Mackwell, 2003; Padrón-Navarta et al., 2014) are orders of magnitude slower on
574 the T-site than M-site.
575 This can be explained, however, by considering the formation reactions of these
576 defects. It becomes clear, below, that these concentration-distance profiles are, in fact,
577 the products of both diffusion (that is, macroscopic movement of H through the
578 crystal) plus point-defect reactions that operate on the unit-cell length scale.
579 In order to form [Mg] at the interface, Mg exchanges with two hydrogen ions:

580



581

582 Then, the defect moves by cation-vacancy exchange of $\{ \text{V}_{\text{Mg}}^{\prime\prime} + 2\text{H}_i^{\bullet} \}$ for $\text{Mg}_{\text{Mg}}^{\times}$.
583 Reaction (7) describes the formation of this defect at the interface, where there is a
584 reservoir to buffer the chemical potentials (i.e., activities) of MgO and H₂O.
585 Hydration of anhydrous Ti^{3+} defects requires hydrogen-vacancy exchange:



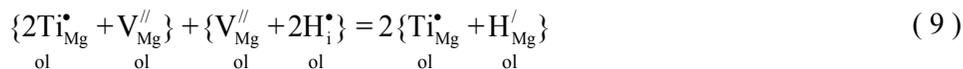
586 After formation, the defect can move by exchange of $\underset{\text{ol}}{\text{V}}_{\text{Mg}}^{\prime\prime} + \underset{\text{ol}}{\text{Mg}}_{\text{Mg}}^{\times}$ for $2\underset{\text{ol}}{\text{H}}_{\text{Mg}}^{\prime}$.

587 Alternatively, interaction between the anhydrous Ti^{3+} defect (considered immobile

588 over the scale of these experiments) and $[\text{Mg}]$ (highly mobile) can also form $[\text{Ti-triv}]$

589 inside the crystal by redistribution of protons:

590



591

592 The choice of mechanism is not clear-cut, but in both cases diffusion of the defect (or

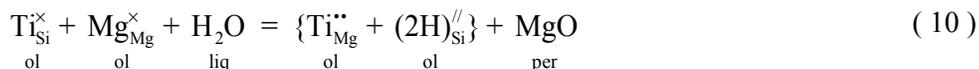
593 formation of the defect by vacancy diffusion and then reaction) is limited to the rate

594 of Mg-vacancy diffusion.

595 To form $[\text{TiCh-PD}]$ from $\text{Mg}_2\text{Ti}^{4+}\text{O}_4$ (anhydrous Ti^{4+}) requires Ti^{4+} to move from the

596 tetrahedral to the octahedral site and be replaced by hydrogen. This necessarily

597 displaces magnesium:



598

599 In order for the defect to then diffuse through the crystal, the $\{\underset{\text{ol}}{\text{Ti}}_{\text{Mg}}^{\bullet\bullet} + (2\underset{\text{ol}}{\text{H}})_{\text{Si}}^{\prime\prime}\}$ could

600 exchange places with an adjacent $\underset{\text{ol}}{\text{Ti}}_{\text{Si}}^{\times} + \underset{\text{ol}}{\text{Mg}}_{\text{Mg}}^{\times}$. However, this involves Mg^{2+} and Ti^{4+}

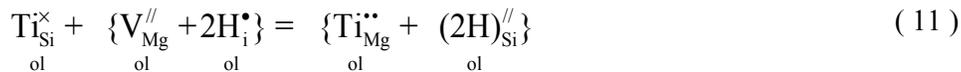
601 exchanging places on the M sites, which is expected to be slower than M-site vacancy

602 diffusion. This diffusion mechanism is not in agreement with the data, which shows

603 that H diffusion associated with the different defects have the same diffusion rate.

604 Alternatively, $\underset{\text{ol}}{\text{Ti}}_{\text{Si}}^{\times}$ could interact with $[\text{Mg}]$

605

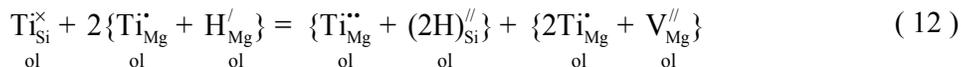


606

607 While these reactions involve the T-site, the macroscopic movement is on the M-site.

608 Or, the anhydrous Ti^{4+} defect could interact with two [Ti-triv], forming one [TiCh-

609 PD] and eliminating both [Ti-triv]:



610

611 For each [TiCh-PD] that is created from the anhydrous Ti^{4+} substitution, a different

612 hydroxylated defect must be available nearby, thus the diffusion rate of H along this

613 defect pathway should be similar to that of [Mg] or [Ti-triv].

614 Reaction (12) is considered more likely in these experiments, given that the

615 concentration of [Ti-triv] is so much higher than that of [Mg] (see Table 2).

616 That the three hydrated point defects observed in these experiments ([TiCh-PD], [Ti-

617 triv] and [Mg]) all propagate at the same rate through the Ti-doped forsterite is

618 explained by the three mechanisms using the same pathway, that of Mg-vacancy

619 diffusion. This interpretation is supported by the similar crystallographic anisotropy

620 of the concentration-distance profiles (longest profiles, hence fastest diffusion, along

621 [001] where M sites are most closely spaced).

622

623 **The effect of chemical activity on diffusion and apparent interface**624 **concentrations**

625

626 Two conditions of $a\text{SiO}_2$ were investigated at 850 °C, 1.5 GPa, by packing the crystal

627 in either forsterite-enstatite or forsterite-periclase.

628 As forming all defects (excluding any direct substitution of 4H^+ for Si^{4+} ; not seen in
629 these experiments) at the interface necessarily liberates MgO (see reactions (10), (8
630) & (7)), it is expected that the hydrogen solubility in the two conditions should
631 differ accordingly. Assuming that the pre-existing anhydrous point defects do not
632 become fully saturated (i.e. fully hydroxylated), the concentrations of all point defects
633 should be higher at higher $a\text{SiO}_2$, and indeed, this is the case (Table 1). At some
634 temperature and pressure, the anhydrous defects should become effectively saturated,
635 then this relationship should no longer hold.

636 This relationship between $a\text{SiO}_2$ and interface concentration is in line with the effect
637 of $a\text{SiO}_2$ on Zr and Hf interface concentrations in olivine in similarly buffered
638 diffusion experiments – higher concentrations at higher $a\text{SiO}_2$ (see Jollands et al.,
639 2014).

640 However, the $a\text{SiO}_2$ of the buffer does not affect the rate of H diffusion. This is in
641 contrast to the effect of $a\text{SiO}_2$ on the diffusion of Zr, Hf, Ni and Co in olivine, where
642 higher $a\text{SiO}_2$ consistently led to faster diffusion (Jollands et al., 2014; Zhukova et al.,
643 2014). This relates to the substitution mechanism of H^+ into the forsterite crystal
644 structure. Given that the diffusing point defect is either $\{\text{V}_{\text{Mg}}^{\prime\prime} + 2\text{H}_i^{\bullet}\}$ or $\{\text{Ti}_{\text{Mg}}^{\bullet} + \text{H}_{\text{Mg}}^{\prime}\}$
645 (which can also be written $\{\text{Ti}_{\text{Mg}}^{\bullet} + \text{V}_{\text{Mg}}^{\prime\prime} + \text{H}_i^{\bullet}\}$), the diffusing hydrogen is always
646 associated with an M-site vacancy. In the case of Zr, Hf, Ni and Co diffusion, the M-
647 site vacancy population of the crystal, whose concentration was imposed by the
648 external buffering assemblage, provided the mechanism for diffusion (i.e. cation-
649 vacancy exchange). In the case of H^+ , the diffusing cation is already associated with
650 its own vacancy. In short, this means that the H^+ does not need to wait for a
651 randomly-walking M-site vacancy in order to make a diffusive jump, hence the

652 overall vacancy concentration of the crystal (imposed by the $a\text{SiO}_2$ buffer) does not
653 appreciably affect the diffusion rate.

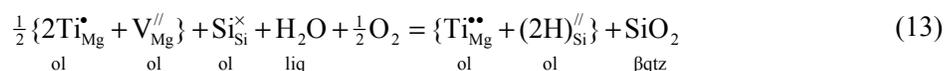
654

655 **The effect of $f\text{O}_2$ on interface concentrations**

656 The starting crystal was prepared at very low oxygen fugacity, where Ti substitutes
657 predominantly in the 3+ oxidation state (Jollands et al., submitted). The conditions
658 under which the hydroxylation were performed (either Re-ReO₂ or Ag-Ag₂O) were
659 very oxidizing, where there should be no detectable Ti³⁺ at equilibrium (e.g.,
660 Mallmann and O'Neill, 2009). Yet, after hydroxylation, hydrated Ti³⁺ is the main
661 hydrous substitution regardless of $f\text{O}_2$ in all the FTIR spectra (except the anomalous
662 “two-slope” profiles), greatly exceeding the amount of Ti⁴⁺ forming the TiCh-PD.
663 Even in the two-slope profiles where some Ti³⁺ is thought to have been oxidized, the
664 Ti³⁺ amount remains high.

665 The reason for this is that oxidation of anhydrous Ti³⁺ to hydrous Ti⁴⁺ (as [TiCh-PD])
666 requires considerable site rearrangement, and the expulsion of Si:

667



668

669 Evidently, these kinetics do not allow the Ti³⁺/ΣTi ratio (at the interface, within the
670 resolution of FTIR spectroscopy) to reach equilibrium; this ratio should be nearly zero
671 at the experimental conditions. It is expected that longer experimental times and/or
672 higher temperatures should allow equilibration of the point defects with the externally
673 buffered conditions, and indeed this has been seen in a similar system (Cr³⁺ and Cr⁴⁺
674 in forsterite; Jollands et al., 2015).

675

676 **Comparison with other studies**

677

678 Several other studies have determined H diffusion coefficients along various
679 pathways in olivine; these are shown in Figure 11 alongside the Arrhenius curves
680 from this study.

681 Given that the mechanisms observed in this study are all interpreted as related to the
682 rate of [Mg] diffusion, it might be expected that the diffusion coefficients of this study
683 should overlap on the Arrhenius plot with those found by Demouchy and Mackwell
684 (2003). However, in the 900-1000 °C range where experiments from this and their
685 study overlap, the diffusion coefficients are around 0.5 orders of magnitude faster in
686 this study. This discrepancy is, however, small given the overall variation of H
687 diffusion in olivine found in the literature. The experiments of Demouchy and
688 Mackwell (2003) were conducted at much lower pressure (using cold-seal apparatus
689 rather than piston cylinder), but the lack of any dependence of pressure on diffusion in
690 this study argues that this should not be significant. Given that H diffuses with its own
691 vacant M-site (i.e. interstitial mechanism), the concentration of M-site vacancies
692 should not affect the rate of diffusion (shown by no effect of $a\text{SiO}_2$ on the diffusion
693 rate). This suggests that the slight increase in diffusion rate relative to that of
694 Demouchy and Mackwell (2003) is not due to the relatively high M-site vacancy
695 concentration related to Ti^{3+} .

696 Padrón-Navarta et al. (2014) synthesised Ti-doped forsterite under hydrous
697 conditions, which were also relatively oxidized, to produce a starting material with H
698 predominantly in [TiCh-PD] and hydroxylated T-vacancies, with minor [Mg] and
699 [triv], which may have been due to minor Ti^{3+} . They then diffused the H out of the
700 crystals at atmospheric pressure, which was monitored not by measuring diffusion

701 profiles (as in this study), but by determining the H associated with each defect type
702 in the bulk crystal. Their results showed that [Mg] and [triv] disappeared rapidly, with
703 implied diffusion rates similar to those found by Demouchy and Mackwell (2003) and
704 in this study (Figure 11). [TiCh-PD], however, were eliminated more slowly, with
705 implied diffusion rates over an order of magnitude slower than in this study (Figure
706 11). Padrón-Navarta et al. (2014) also found that after [TiCh-PD]s were eliminated,
707 the rate of decrease of the hydroxylated T-site defects almost ceased. Their study thus
708 showed that the rate of diffusion of H out of the crystals was dependent on the fastest
709 available mechanism. After the elimination of the (presumed) [triv] defects, there is
710 no mechanism to transfer the [TiCh-PD] locally to a fast diffusion mechanism (i.e.,
711 the reverse of reaction (12)), which explains the apparently slower rate of diffusion.
712 This assertion could be tested by measuring H diffusion into forsterite doped with
713 small amounts of Ti^{4+} and no Ti^{3+} or other trivalent cations if such material were to
714 become available. We expect that in the absence of any hydroxylated trivalent defects,
715 H diffusion (diffusion-in) along the [TiCh-PD] pathway would be considerably slower
716 than observed in this study.

717

718 **Implications**

719

- 720 1. Hydrogen diffusion is slightly faster in Ti-doped forsterite than in pure
721 forsterite. The presence in natural olivines of trace elements with an affinity
722 for H^+ (e.g. trivalent cations on the M-sites) should be considered when
723 projecting experimentally determined diffusion coefficients into natural
724 systems.

- 725 2. The chemical activity and oxygen fugacity of the surroundings does not affect
726 the rate of H-diffusion in olivine, along the M-site pathway. Frozen H-
727 diffusion profiles in natural xenocrysts can be used to determine timescales of
728 residence/ascent regardless of the silica saturation or undersaturation of the
729 magma.
- 730 3. Diffusion in systems that require charge balance is a composite problem of
731 both (a) *diffusion* of vacancies/charge-balancing agents and the diffusing
732 species and (b) *reactions* resulting in rearrangement of site occupancy. Whilst
733 diffusion-in (from this study) and diffusion-out (from Padrón-Navarta et al.,
734 2014) coefficients are significantly different, no different *diffusion*
735 mechanisms are needed to describe this. The difference in apparent *diffusion*
736 rates is instead a function of the difference in *reaction* mechanisms. In systems
737 that require charge-balance, it may be necessary to consider both diffusion and
738 reaction when attempting to describe diffusion rate.

739

740 **Acknowledgements**

741 The authors wish to thank Rachel Stott and Pete Tollan for early assistance with FTIR
742 spectroscopy, Jeremy Wykes, Jung Woo Park, Maria Rosa Scicchitano, Michael
743 Schwartz, Dave Clark and Dean Scott for various general help, Uli Faul and Andrew
744 Berry for useful comments regarding Ti clinohumite defects, and Colin MacRae of
745 CSIRO for providing OpticalFit software. The manuscript was greatly improved
746 through constructive reviews by Elizabeth Ferriss and an anonymous reviewer, with
747 editorial handling by Thomas Mueller.

748

749

Calibration used	Absorption coefficient		
	[TiCh-PD]	[Ti-triv]	[Mg]
Bell et al. (2003)	0.188 ± 0.012	0.188 ± 0.012	0.188 ± 0.012
Kovács et al. (2010)	0.18 ± 0.07	0.18 ± 0.05	0.03 ± 0.03
Bell et al (2003) & Libowitzky and Rossmann (1997)	0.188 ± 0.012	0.083 ± 0.014	0.056 ± 0.009
Withers et al. (2012)	0.119 ± 0.006	0.119 ± 0.006	0.119 ± 0.006

750

751 Table 1: Different determinations of absorption coefficients can have a considerable effect on
 752 calculations of the concentration of H₂O. Bell et al (2003) assume all defects have the same coefficient,
 753 but their samples were dominated by defects in the [TiCh-PD] wavenumber range. Kovács et al (2010)
 754 does not make this assumption but did not include absolute (standardless) measurements of hydrogen
 755 concentration. Their samples included defects in the [Mg] and [TiCh-PD] range, along with trivalent
 756 cation associated H (using Sc³⁺). Withers et al (2012) assumes the same coefficient for all defects, with
 757 synthetic crystals dominated by bands in the [TiCh-PD] and [Mg] wavenumber range (although their
 758 spectra were dominated by [Si] defect bands). Also given is the Bell et al (2003) coefficient (assumed
 759 correct for [TiCh-PD] adjusted for lower wavenumbers using the Libowitzky and Rossmann (1997)
 760 relationship. Considerable uncertainty still exists in absorption coefficients, hence in this study we refer
 761 primarily to the integrated peak area rather than wt. ppm H₂O.

762

I.D. (this study)	I.D. (SESAR)	T (°C)	P (GPa)	t (hr)	fO ₂ buffer	aSiO ₂ buffer	Sample thickness (µm)	log ₁₀ diffusion coefficients (m ² s ⁻¹)					Normalised Integrated absorbance at interface (cm ⁻²)		
								logD _[001] [TiCH-PD]	logD _[001] [Ti-triv]	logD _[001] [Mg]	logD _[001] (total)	logD _[100] (total)	[TiCh-PD]	[Ti-triv]	[Mg]
hydrol8	IEMC J0007	650	1.5	360	Re-ReO ₂	fo-ens	448±20	N.D.	-14.8 ±0.1	N.D.	-14.8 ±0.1*	-15.8 ±0.2*	12 ± 2	7.7 ± 0.7	N.D.
hydrol2	IEMC J0002	750	1.5	24	Re-ReO ₂	fo-ens	261±14	N.D.	-14.0 ±0.3	N.D.	-14.0 ±0.3*	N.D.	N.D.	0.2 ± 0.2	N.D.
hydrol1	IEMC J0001	850	1.5	6	Re-ReO ₂	fo-ens	567±10	-12.4 ±0.1	-12.4 ±0.1	-12.5 ±0.2	-12.5 ±0.1	-13.5 ±0.1	18 ± 1	51 ± 7	9 ± 4
hydrol6	IEMC J0005	850	1.5	12	Ag-Ag ₂ O	fo-ens	536±10	-12.3 ±0.1	-12.6 ±0.1	-12.4 ±0.1	-12.5 ±0.1	-13.3 ±0.1	16 ± 1	51 ± 4	6 ± 0.5
hydrol7	IEMC J0006	850	1.5	12	Re-ReO ₂	fo-per	652±17	-12.6 ±0.1	-12.6 ±0.2	-12.7 ±0.1	-12.5 ±0.1		14 ± 2	28 ± 2	7 ± 1
hydrol4	IEMC J0004	850	2.5	12	Re-ReO ₂	fo-ens	605±16	-12.3 ±0.1	-12.6 ±0.1	-12.7 ±0.2	-12.6 ±0.1	-13.4 ±0.1	29 ± 5	81 ± 12	28 ± 5
hydrol3	IEMC J0003	950	1.5	3	Re-ReO ₂	fo-ens	499±12	-12.0 ±0.2	-11.9 ±0.1	-11.8 ±0.1	-11.9 ±0.2	-12.8 ±0.2	28 ± 3	74 ± 5	21 ± 2
hydrol10	IEMC J0008	1000	1.5	1	Re-ReO ₂	fo-ens	436±12	-11.4 ±0.1	-11.5 ±0.1	-11.6 ±0.1	-11.5 ±0.2	-12.1 ±0.2	20 ± 10	102 ± 2	31 ± 2

763

764 Table 2: Experimental conditions and results. Thicknesses are average and 1 standard deviation of thicknesses determined from all points measured in the crystal. SESAR ID
 765 are International Geo Sample Numbers (IGSNs) compiled at <http://www.geosamples.org>. The diffusion coefficients (all log₁₀D) are determined from summed absorbance
 766 (sum of integrated areas from all three defects). Diffusion rates are determined along the [001] (logD_[001]) and [100] (logD_[100]) axes, all measured in the (010) plane using
 767 unpolarised light. Integrated absorbance values are taken looking down the [010] direction. No correction is made for defect polarization – values corrected using Equations
 768 1-3 are given in Table 3. Errors on diffusion coefficients and integrated absorbance are (subjectively) determined from data scatter around error function, or 0.1, whichever is
 769 greater. *Diffusion coefficient determined using Ti³⁺ peak only. N.D.: not determined, peak too small.

I.D. (this study)	Total normalized integrated absorbance at interface (cm^{-2})			wt. ppm H_2O (interface)			
	[TiCh-PD]	[Ti-triv]	[Mg]	B03	K10	W12	B03+ LR
hydrol8	24 ± 4	18 ± 2		7.7 ± 1.2	7.4 ± 2.7	4.9 ± 0.7	5.9 ± 1.1
hydrol2		0.5 ± 0.5		0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	0 ± 0
hydrol1	35 ± 2	116 ± 16	19 ± 8	32.1 ± 5.5	27.9 ± 9.6	20.3 ± 3.3	17.4 ± 3.2
hydrol6	32 ± 2	116 ± 9	13 ± 1	30.1 ± 3	27 ± 8.7	19.1 ± 1.7	16.3 ± 2.5
hydrol7	28 ± 4	64 ± 5	15 ± 2	19.9 ± 2.4	16.9 ± 5.8	12.6 ± 1.4	11.3 ± 2
hydrol4	57 ± 10	185 ± 27	59 ± 10	56.5 ± 9.7	45.3 ± 16.6	35.7 ± 6	29.3 ± 6.2
hydrol3	55 ± 6	169 ± 11	44 ± 4	50.3 ± 5.2	41.6 ± 14	31.9 ± 3	26.8 ± 4.3
hydrol10	39 ± 20	233 ± 5	65 ± 4	63.3 ± 7.8	50.9 ± 18.1	40.1 ± 4.5	30.3 ± 7.6

770

771

772

773

774

775

776

777

778

779

780

781

782

783

784

785

786

787

788

789

790

791

792

793

794

795

796

797

798

799

799

Table 3: Interface total absorbance and H_2O concentration. Total normalized integrated absorbance values are corrected from those in Table 2 for orientation using the relationships presented in Equations 1-3, then converted into wt. ppm H_2O using the absorption coefficients detailed in Table 1.

Figure 1: Laser ablation ICP-MS transects across the starting material. The Ti profile has ~100 ppm variation from core to rim along [001]. Also note the change in Al concentration; Al shows a step from around 8 to 14 ppm. The dip in concentration at the centre of the [001] profile is from ablating over the pre-existing laser track along [100].

Figure 2: Experimental design. Top: schematic diagram of thick-walled, swaged Ag capsule containing a solid state $f\text{O}_2$ buffer, a chemical activity buffer (forsterite + enstatite or periclase) and one or two oriented cubes of Ti-doped forsterite. Middle: capsule after experiment showing swelling; this suggests that pressure is hydrostatic inside the capsule, protecting the crystal from impingement or shearing. Bottom: transmitted light image of a double polished forsterite crystal post-experiment (hydrol1).

Figure 3: A spectrum from the infrared OH stretching (normalized to 1 cm thickness) region resolved into Gaussian distributions. Parameters a, b and c (inset table) reflect the position, width and height of the curves according to the Gaussian equation. The main peak at 3351 cm^{-1} is resolved into two, with a lower, slightly broader peak at 3349 cm^{-1} giving a lower wavenumber shoulder. The low peak at 3252 cm^{-1} is added to compensate for poor baseline subtraction in this region. Also shown are residuals between spectrum (black line) and simulation (red dotted line).

Figure 4: Left: Polarised, principal axis spectra taken from the interface ($50 \times 50\ \mu\text{m}$ aperture) of experiment hydrol 4 (2 perpendicular cuts), normalized to 1 cm thickness. Right: polar plots of each defect (three rows) taken in two perpendicular cuts (two columns). [TiCh-PD] is almost absent when the crystal is cut parallel to (100), hence this plot is missing. [Ti-triv] is comprised of two peaks with the opposite polarization.

800 Figure 5: Logarithm of integrated absorbance (unpolarised light, normalized to 1 cm
801 thickness, not corrected for orientation) at the crystal edge as a function of inverse
802 temperature. a) individual defects, all fo-ens buffered. [Ti-triv] and [Mg] show
803 exponential increases, [TiCh-PD] does not. b) total absorbance. Oxygen fugacity does
804 not affect interfaces but pressure and $a\text{SiO}_2$ have an effect (850 °C data).

805 Figure 6: The effect of $a\text{SiO}_2$ and $f\text{O}_2$ on FTIR spectra (left) and diffusion profiles
806 (right). The [Ti-triv] peak (3351 cm^{-1}) remains, even in very oxidized conditions, with
807 no change between Ag-Ag₂O and Re-ReO₂ buffered conditions.

808 Figure 7: Variation in unpolarised IR spectra in the O-H stretching region across
809 [001] of hydrol10 (1000 °C experiment). For clarity, this is a subsample (~25 %) of
810 the total number of measurements from this axis. All spectra are normalized to 1cm
811 thickness using integrated area of Si-O bands ($1625\text{-}2150\text{ cm}^{-1}$) to eliminate artifacts
812 from polishing on cloth (causing the crystal to be thinner at the edges).

813 Figure 8: Hydrol3 (950 °C experiment) mapped in unpolarised light with 50x50 μm
814 aperture, 30 μm step. Top: map of integrated area under trivalent peaks extracted from
815 Bruker OPUS software, scaled between 0-90. The edge of the crystal appears white
816 due to spectral contamination from epoxy resin. Middle: [001] profile extracted from
817 map, including fits of integrated area underneath the [Ti-triv], [TiCh-PD] and [Mg]
818 peaks to equation (4). Bottom: [100] profile extracted and treated in the same way.
819 The large aperture and step size in mapping mode is not fully appropriate for such
820 short profiles; diffusivity is underestimated.

821
822 Figure 9: Example of an [001] profile (hydrol4) showing asymmetry. The right hand
823 side of the profile allows fits to the error function for each individual defect. The left
824 hand side does not; the steep inflection in [TiCh-PD] concentration at the interface
825 precludes fits to a single error function. The left side of the profile also includes a
826 short diffusion profile of a peak at 3428 cm^{-1} . Interface spectra are also shown; the
827 spectrum from the left has lower [Ti-triv] and higher [TiCh-PD] and [Mg] than the
828 right hand spectrum, as well as the peak at 3428 cm^{-1} . Also note that the left side
829 suffers from a higher baseline in the [TiCh-PD] region.

830 Figure 10: The effect of pressure on diffusion along [001] and incorporation of
831 hydrogen. From 1.5 to 2.5 GPa, the total OH solubility increases by 60-80 %. The
832 concentration increase is taken up by [Mg] and [Ti-triv] defects; there is no increase
833 in [TiCh-PD] concentration. Any change in the rate of diffusion with pressure is less
834 than the uncertainty in the measurements.

835 Figure 11: Arrhenius plot of H diffusion in Ti-doped forsterite along the [001] (black
836 circles) and [100] (grey circles). Solid black lines are fits to $D=D_0\exp(E_a/RT)$,
837 assuming that E_a (activation energy of diffusion) is the same along both axes. Also
838 shown are data from M&K90: proton-polaron exchange; Mackwell and Kohlstedt
839 (1990), DF12: H-D exchange, [100], natural olivine; DuFrane (2012), D&M(03):
840 hydrogen- M-site vacancy coupled diffusion (forsterite); Demouchy and Mackwell
841 (2003), D&M(06): hydrogen- M-site vacancy coupled diffusion (natural olivine);
842 Demouchy and Mackwell (2006), I&B(06): H-D exchange, [001], near pure forsterite;
843 Ingrin and Blanchard (2006). PN(14): Diffusion out of H from H±Ti doped forsterite;
844 Padrón-Navarta et al. (2014).

845

846 **References**

847

- 848 Assal, J., Hallstedt, B., and Gauckler, L.J. (1997). Thermodynamic assessment of the silver–oxygen
849 system. *Journal of the American Ceramic Society*, 80, 3054-3060.
- 850 Balan, E., Ingrin, J., Delattre, S., Kovács, I., and Blanchard, M. (2011) Theoretical infrared spectrum of
851 OH-defects in forsterite. *European Journal of Mineralogy*, 23, 285-292.
- 852 Bell, D.R., and Rossman, G.R. (1992) Water in Earth's Mantle: The Role of Nominally Anhydrous
853 Minerals. *Science*, 255, 1391-1397.
- 854 Bell, D.R., Rossman, G.R., Maldener, J., Endisch, D., and Rauch, F. (2003) Hydroxide in olivine: a
855 quantitative determination of the absolute amount and calibration of the IR spectrum. *Journal of*
856 *Geophysical Research: Solid Earth*, 108.B2.
- 857 Bell, D.R., Rossmann, G.R., and Moore, R.O. (2004) Abundance and Partitioning of OH in a High-
858 pressure Magmatic System: Megacrysts from the Monastery Kimberlite, South Africa. *Journal of*
859 *Petrology*, 45, 1539-1564.
- 860 Beran, A. (1969) Über (OH)-Gruppen in Olivin. *Oesterr Akad Wiss Math Naturwiss Kl Anzeiger*, 73-
861 74 (in German).
- 862 Berry, A.J., Hermann, J., O'Neill, H.S.C., and Foran, G.J. (2005) Fingerprinting the water site in
863 mantle olivine. *Geology*, 33, 869-872.
- 864 Berry, A.J., O'Neill, H.S.C., Hermann, J., and Scott, D.R. (2007a) The infrared signature of water
865 associated with trivalent cations in olivine. *Earth and Planetary Science Letters*, 261, 134-142.
- 866 Berry, A.J., Walker, A.M., Hermann, J., O'Neill, H.S.C., Foran, G.J., and Gale, J.D. (2007b) Titanium
867 substitution mechanisms in forsterite. *Chemical Geology*, 242, 176-186.
- 868 Bolfan-Casanova, N. (2005) Water in the Earth's mantle. *Mineralogical Magazine*, 69, 229-257.
- 869 Carslaw, H.S., and Jaeger, J.C. (1959) *Conduction of heat in solids*. Oxford: Clarendon Press, United
870 Kingdom.
- 871 Chakraborty, S., Farver, J.R., Yund, R.A., and Rubie, D.C. (1994) Mg Tracer Diffusion in Synthetic
872 Forsterite and San-Carlos Olivine as a Function of P, T and fO_2 . *Physics and Chemistry of Minerals*,
873 21, 489-500.
- 874 Chakraborty, S. (1997) Rates and mechanisms of Fe-Mg interdiffusion in olivine at 980 degrees-1300
875 degrees C. *Journal of Geophysical Research-Solid Earth*, 102, 12317-12331.
- 876 Crank, J. (1975) *The Mathematics of Diffusion*. Oxford University Press, Oxford.
- 877 Crepisson, C., Bureau H., Blanchard M., Ingrin J., and Balan E. (2014) Theoretical infrared spectrum
878 of partially protonated cationic vacancies in forsterite. *European Journal of Mineralogy*, 26, 203-210.
- 879 Demouchy, S., and Mackwell, S. (2003) Water diffusion in synthetic iron-free forsterite. *Physics and*
880 *Chemistry of Minerals*, 30, 486-494.
- 881 Demouchy, S., Jacobsen, S.D., Gaillard, F., and Stern, C.R. (2006) Rapid magma ascent recorded by
882 water diffusion profiles in mantle olivine. *Geology*, 34, 429-432.
- 883 Demouchy, S., and Mackwell, S. (2006) Mechanisms of hydrogen incorporation and diffusion in iron-
884 bearing olivine. *Physics and Chemistry of Minerals*, 33, 347-355.
- 885 Demouchy, S., and Bolfan-Casanova, N. (2016). Distribution and transport of hydrogen in the
886 lithospheric mantle: A review. *Lithos*, 240–243, 402-425.
887
- 888 Denis, C.M., Demouchy, S., and Shaw, C.S. (2013) Evidence of dehydration in peridotites from Eifel
889 Volcanic Field and estimates of the rate of magma ascent. *Journal of Volcanology and Geothermal*
890 *Research*, 258, 85-99.

- 891 Dohmen, R., Chakraborty, S., and Becker, H.-W. (2002) Si and O diffusion in olivine and implications
892 for characterizing plastic flow in the mantle. *Geophysical Research Letters*, 29, 2030.
- 893 Dohmen, R., and Chakraborty, S. (2007) Fe-Mg diffusion in olivine II: point defect chemistry, change
894 of diffusion mechanisms and a model for calculation of diffusion coefficients in natural olivine (vol 34,
895 pg 409, 2007). *Physics and Chemistry of Minerals*, 34, 597-598.
- 896 Du Frane, W.L., and Tyburczy, J.A. (2012) Deuterium-hydrogen exchange in olivine: Implications for
897 point defects and electrical conductivity. *Geochemistry, Geophysics, Geosystems*, 13.
- 898 Ferriss, E., Plank, T., Walker, D., and Nettles, M. (2015). The whole-block approach to measuring
899 hydrogen diffusivity in nominally anhydrous minerals. *American Mineralogist*, 100, 837-851.
- 900 Grant, K., Ingrin, J., Lorand, J.P., and Dumas, P. (2007) Water partitioning between mantle minerals
901 from peridotite xenoliths. *Contributions to Mineralogy and Petrology*, 154, 15-34.
- 902 Hack, A.C., and Mavrogenes, J.A. (2006) A cold-sealing capsule design for synthesis of fluid
903 inclusions and other hydrothermal experiments in a piston-cylinder apparatus. *American Mineralogist*,
904 91, 203-210.
- 905 Hermann, J., Fitz Gerald, J.D., Malaspina, N., Berry, A.J., and Scambelluri, M. (2007) OH-bearing
906 planar defects in olivine produced by the breakdown of Ti-rich humite minerals from Dabie Shan
907 (China). *Contributions to Mineralogy and Petrology*, 153, 417-428.
- 908 Hirschmann, M.M., Aubaud, C., and Withers, A.C. (2005) Storage capacity of H₂O in nominally
909 anhydrous minerals in the upper mantle. *Earth and Planetary Science Letters*, 236, 167-181.
- 910 Jochum, K.P., Weis, U., Stoll, B., Kuzmin, D., Yang, Q., Raczek, I., Jacob, D.E., Stracke, A., Birbaum,
911 K., Frick, D.A., Günther, D., and Enzweiler, J. (2011) Determination of Reference Values for NIST
912 SRM 610–617 Glasses Following ISO Guidelines. *Geostandards and Geoanalytical Research*, 35, 397-
913 429.
- 914 Jollands, M.C., O'Neill, H.S.C., and Hermann, J. (2014) The importance of defining chemical
915 potentials, substitution mechanisms and solubility in trace element diffusion studies: the case of Zr and
916 Hf in olivine. *Contributions to Mineralogy and Petrology*, 168, 1-19.
- 917 Jollands, M.C., O'Neill, H.S.C., Hermann, J., Berry A.J., and Rivard, C. (2015) Hydrogen Diffusion in
918 Cr-Doped Forsterite Studied by XANES and FTIR. *Goldschmidt Abstracts*, 1470.
- 919 Kitamura, M., Kondoh, S., Morimoto, N., Miller, G.H., Rossman, G.R., and Putnis, A. (1987) Planar
920 OH-bearing defects in mantle olivine. *Nature*, 328, 143-145.
- 921 Koch-Muller, M., Matsyuk, S., Rhede, D., Wirth, R., and Khisina, N. (2006) Hydroxyl in mantle
922 olivine xenocrysts from the Udachnaya kimberlite pipe. *Physics and Chemistry of Minerals*, 33, 276-
923 287.
- 924 Kohlstedt, D.L., and Mackwell, S.J. (1998) Diffusion of hydrogen and intrinsic point defects in olivine.
925 *Zeitschrift für physikalische Chemie*, 207, 147-162.
- 926 Kovács, I., O'Neill, H.S.C., Hermann, J., and Hauri, E (2010) Site-specific infrared O-H absorption
927 coefficients for water substitution into olivine. *American Mineralogist*, 95, 292-299.
- 928 Libowitzky, E., and Rossman, G. R. (1997). An IR absorption calibration for water in minerals.
929 *American Mineralogist*, 82, 1111-1115.
- 930 Mackwell, S.J., and Kohlstedt, D.L. (1990) Diffusion of hydrogen in olivine: Implications for water in
931 the mantle. *Journal of Geophysical Research: Solid Earth*, 95, 5079-5088.
- 932 MacRae, C.M., and Wilson, N.C. (2008) Luminescence database I: minerals and materials. *Microscopy
933 and Microanalysis*, 14, 184-204.
- 934 Mallmann, G., and O'Neill, H.S.C. (2009) The Crystal/Melt Partitioning of V during Mantle Melting as
935 a Function of Oxygen Fugacity Compared with some other Elements (Al, P, Ca, Sc, Ti, Cr, Fe, Ga, Y,
936 Zr and Nb). *Journal of Petrology*, 50, 1765-1794.
- 937 Miller, G., Rossman, G., and Harlow, G. (1987) The natural occurrence of hydroxide in olivine.
938 *Physics and Chemistry of Minerals*, 14, 461-472.
- 939 Padrón-Navarta, J.A., Hermann, J., and O'Neill, H.S.C. (2014) Site-specific hydrogen diffusion rates in
940 forsterite. *Earth and Planetary Science Letters*, 392, 100-112.

- 941 Paton, C., Hellstrom, J., Paul, B., Woodhead, J., and Hergt, J. (2011) Iolite: Freeware for the
942 visualisation and processing of mass spectrometric data. *Journal of Analytical Atomic Spectrometry*,
943 26, 2508-2518.
- 944 Peslier, A.H., and Luhr, J.F. (2006) Hydrogen loss from olivines in mantle xenoliths from Simcoe
945 (USA) and Mexico: Mafic alkalic magma ascent rates and water budget of the sub-continental
946 lithosphere. *Earth and Planetary Science Letters*, 242, 302-319.
- 947 Peslier, A.H., Woodland, A.B., and Wolff, J.A. (2008) Fast kimberlite ascent rates estimated from
948 hydrogen diffusion profiles in xenolithic mantle olivines from southern Africa. *Geochimica
949 Cosmochimica Acta*, 72, 2711-2722.
- 950 Peslier, A.H., and Bizimis, M. (2015) Water in Hawaiian peridotite minerals: A case for a dry
951 metasomatized oceanic mantle lithosphere. *Geochemistry, Geophysics, Geosystems*,
952 doi:10.1002/2015GC005780
- 953 Peslier, A.H., Bizimis, M., and Matney, M. (2015) Water disequilibrium in olivines from Hawaiian
954 peridotites: Recent metasomatism, H diffusion and magma ascent rates. *Geochimica Cosmochimica
955 Acta*, 154, 98-117.
- 956 Pownceby, M. I., and O'Neill, H.S.C. (1994). Thermodynamic data from redox reactions at high
957 temperatures. IV. Calibration of the Re-ReO₂ oxygen buffer from EMF and NiO+ Ni-Pd redox sensor
958 measurements. *Contributions to Mineralogy and Petrology*, 118, 130-137.
- 959 Skogby, H., and Rossman, G.R. (1991). The intensity of amphibole OH bands in the infrared
960 absorption spectrum. *Physics and Chemistry of Minerals*, 18, 64-68.
- 961 Shen, T., Hermann, J., Zhang, L., Padrón-Navarta, J.A., and Chen, J. (2014) FTIR spectroscopy of Ti-
962 chondrodite, Ti-clinohumite, and olivine in deeply subducted serpentinites and implications for the
963 deep water cycle. *Contributions to Mineralogy and Petrology*, 167, 1-15.
- 964 Smyth, J., Frost, D., Nestola, F., Holl, C., and Bromiley, G. (2006) Olivine hydration in the deep upper
965 mantle: effects of temperature and silica activity. *Geophysical Research Letters*, 33.
- 966 Thoraval, C., and Demouchy, S. (2014) Numerical models of ionic diffusion in one and three
967 dimensions: application to dehydration of mantle olivine. *Physics and Chemistry of Minerals*, 1-15
- 968 Umemoto, K., Wentzcovitch, R. M., Hirschmann, M. M., Kohlstedt, D. L., and Withers, A. C. (2011).
969 first-principles investigation of hydrous defects and IR frequencies in forsterite: The case for Si
970 vacancies. *American Mineralogist*, 96, 1475-1479.
- 971 Walker, A.M., Hermann, J., Berry, A.J., and O'Neill, H.S.C. (2007) Three water sites in upper mantle
972 olivine and the role of titanium in the water weakening mechanism. *Journal of Geophysical Research:
973 Solid Earth*, 112, B05211.
- 974 Wirth, R., Dobrzhinetskaya, L.F., and Green, H.W. (2001) Electron microscope study of the reaction
975 olivine plus H₂O+TiO₂ = titanian clinohumite plus Titanian chondrodite synthesized at 8 GPa, 1300 K.
976 *American Mineralogist*, 86, 601-610.
- 977 Withers, A.C., Bureau, H., Raepsaet, C., and Hirschmann, M.M. (2012) Calibration of infrared
978 spectroscopy by elastic recoil detection analysis of H in synthetic olivine. *Chemical Geology*, 334, 92-
979 98.
- 980 Zhang, F., and Wright, K. (2010) Coupled (H⁺,M³⁺) substitutions in forsterite. *Geochimica
981 Cosmochimica Acta*, 74, 5958-5965.
- 982 Zhang, Z., and Duan, Z. (2005) Prediction of the PVT properties of water over wide range of
983 temperatures and pressures from molecular dynamics simulation. *Physics of the Earth and Planetary
984 Interiors*, 149, 335-354.
- 985 Zhukova, I., O'Neill, H.S.C., Cambell, I.H., and Kilburn, M.R. (2014) The effect of silica activity on
986 the diffusion of Ni and Co in olivine. *Contributions to Mineralogy and Petrology*, 168, 1-15.
- 987
988
- 989

Figure 1

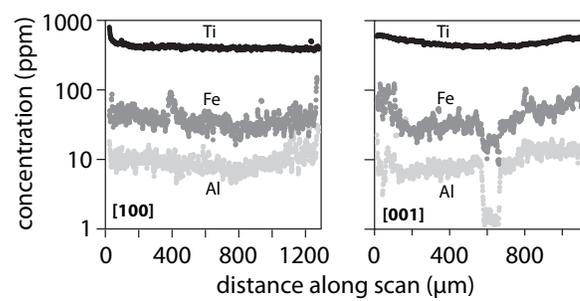


Figure 2

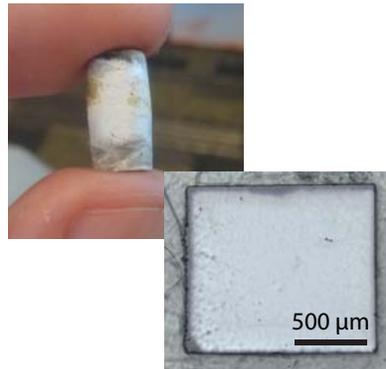
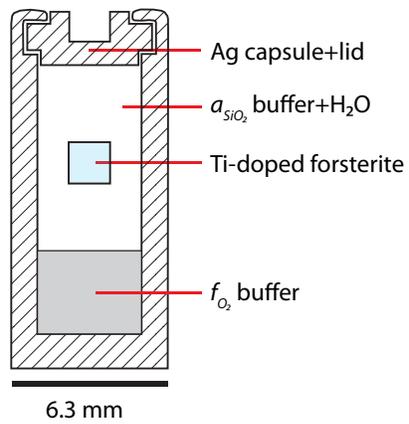


Figure 3

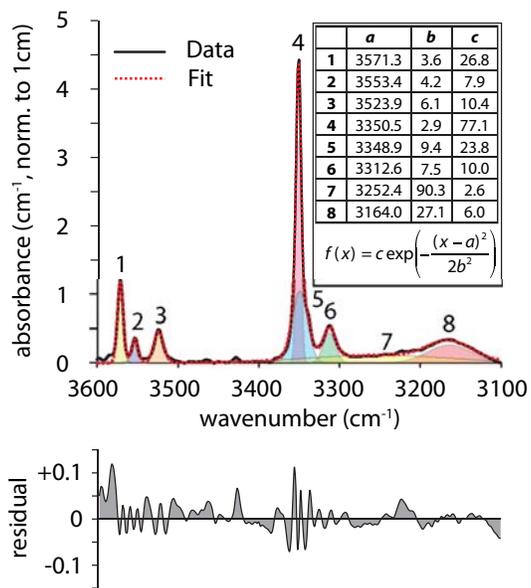


Figure 4

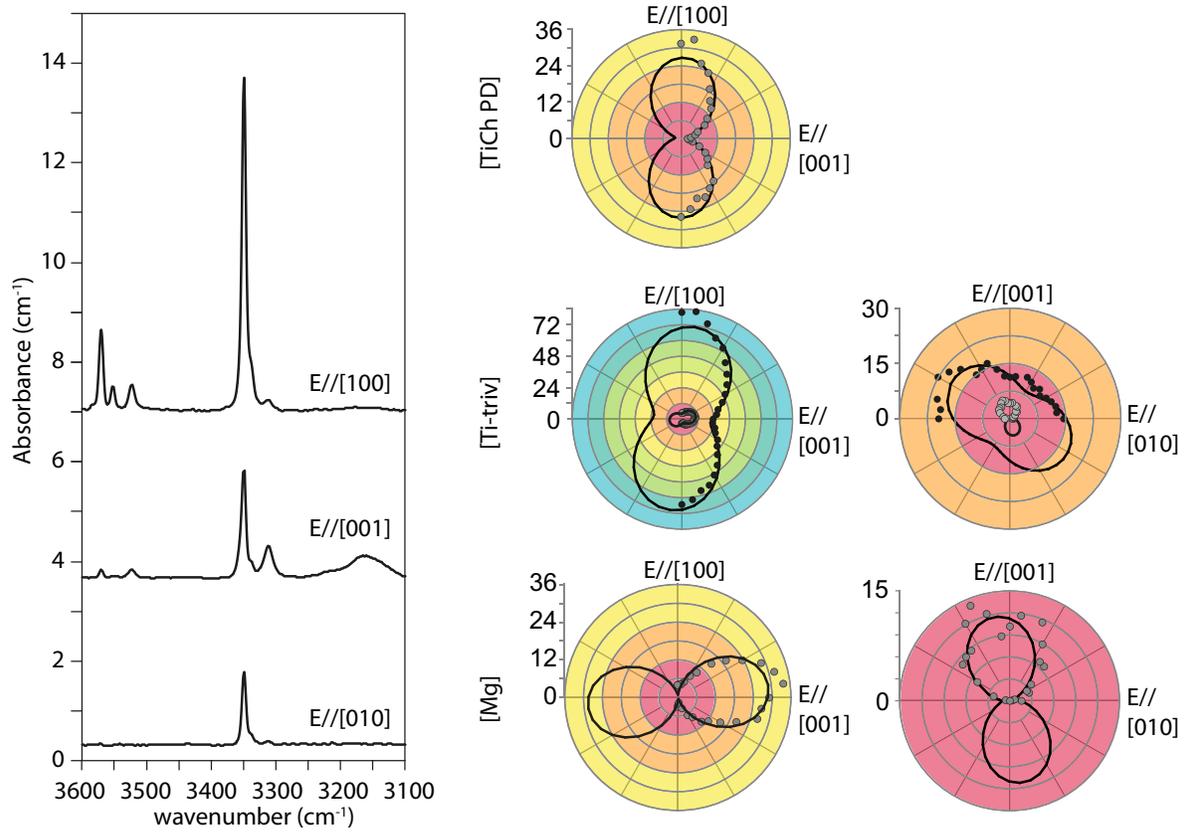


Figure 5

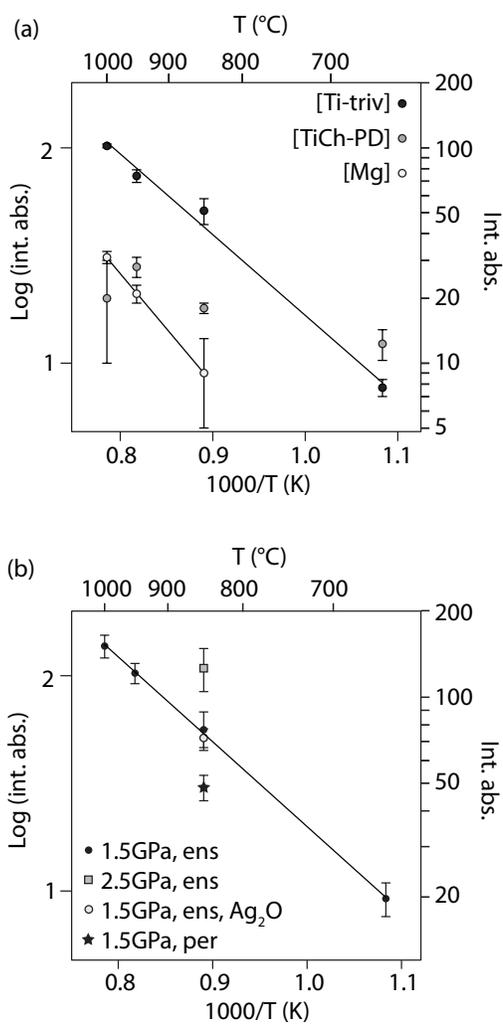


Figure 6

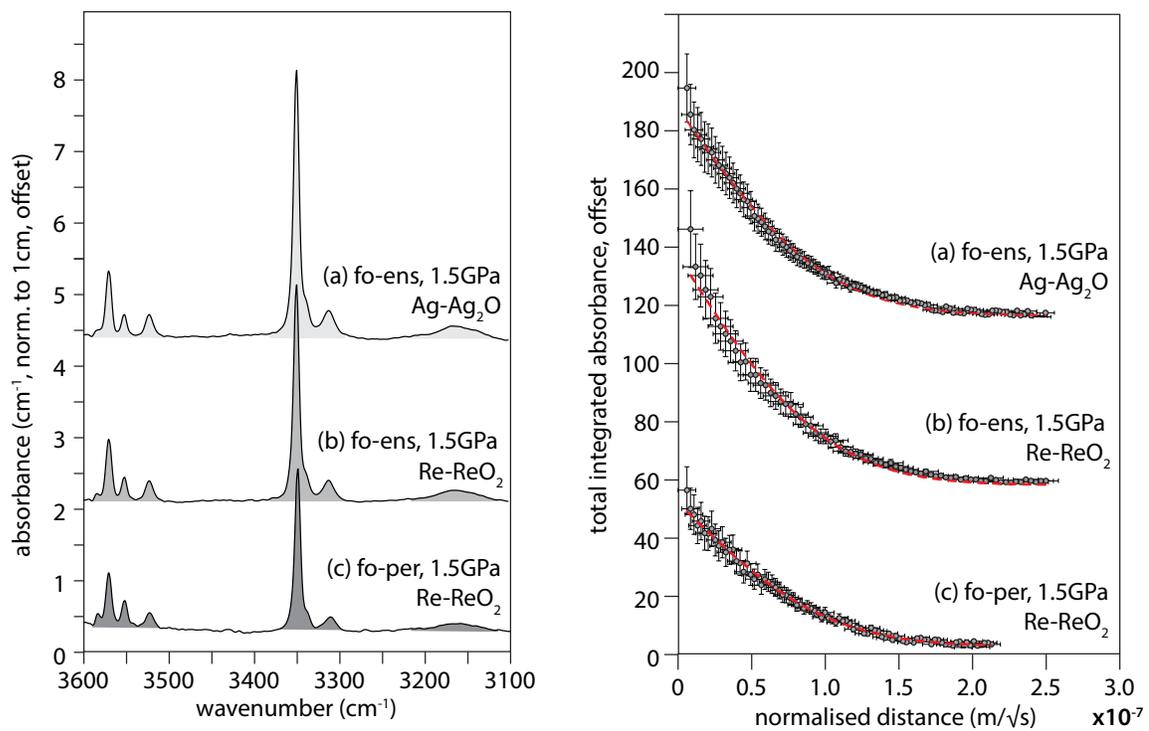


Figure 7

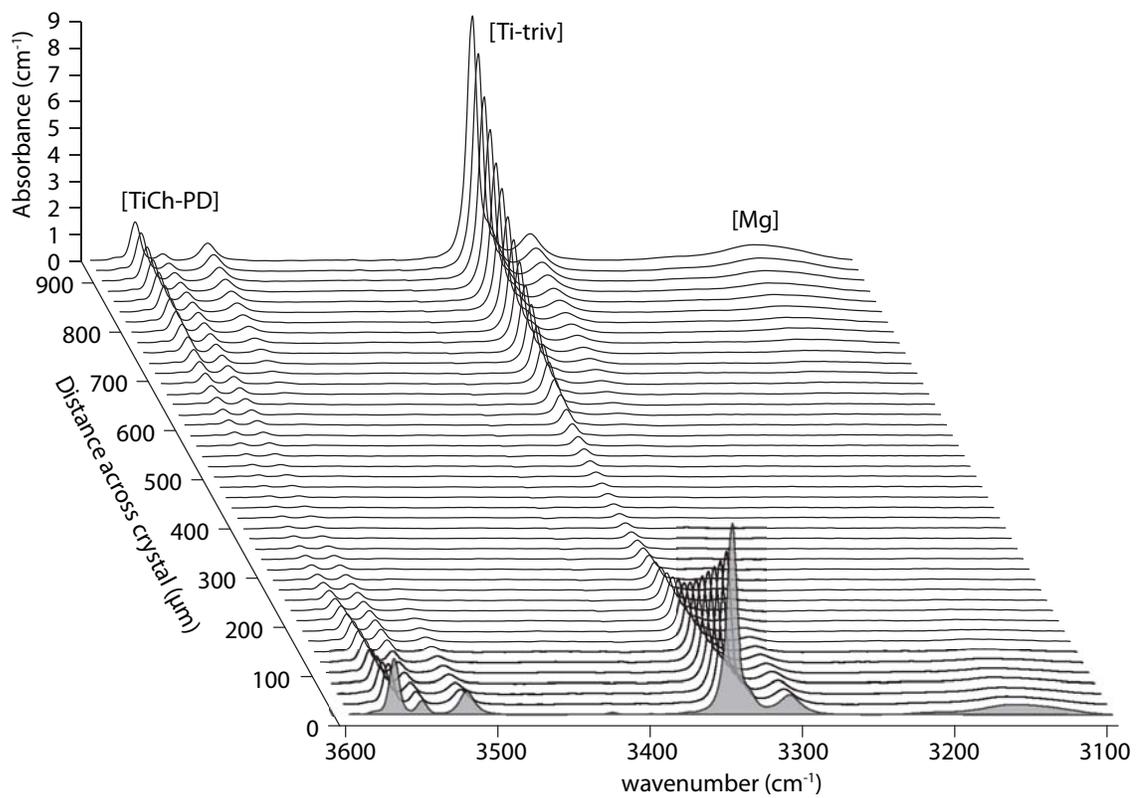


Figure 8

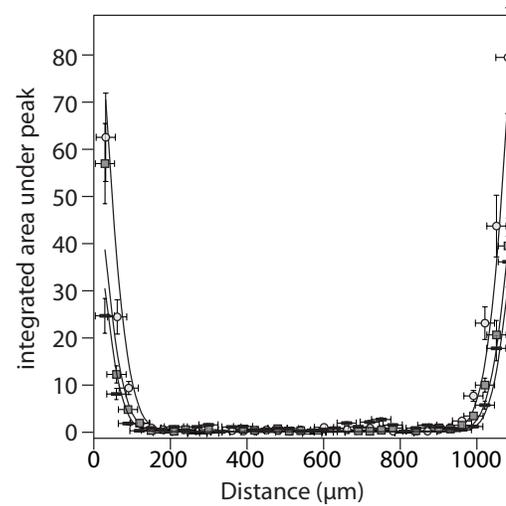
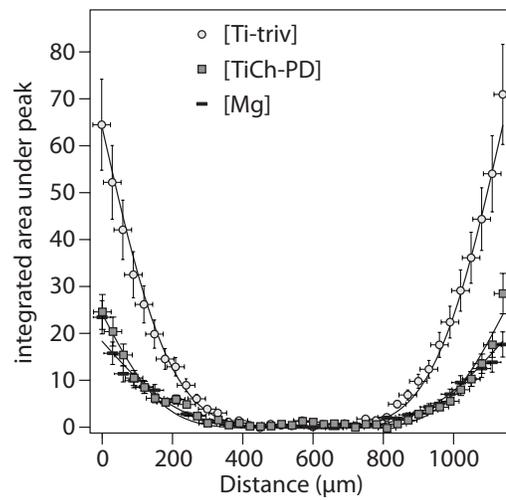
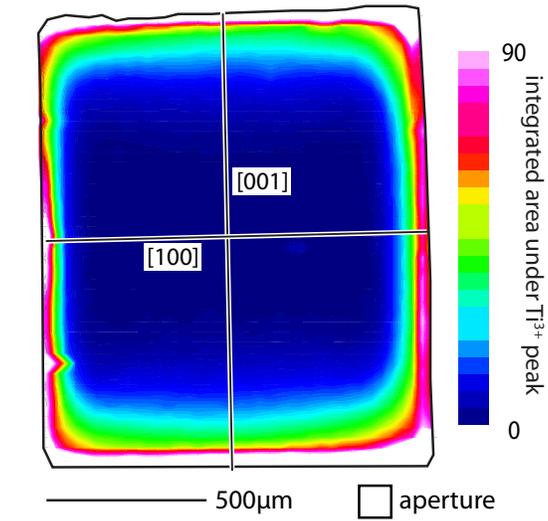


Figure 9

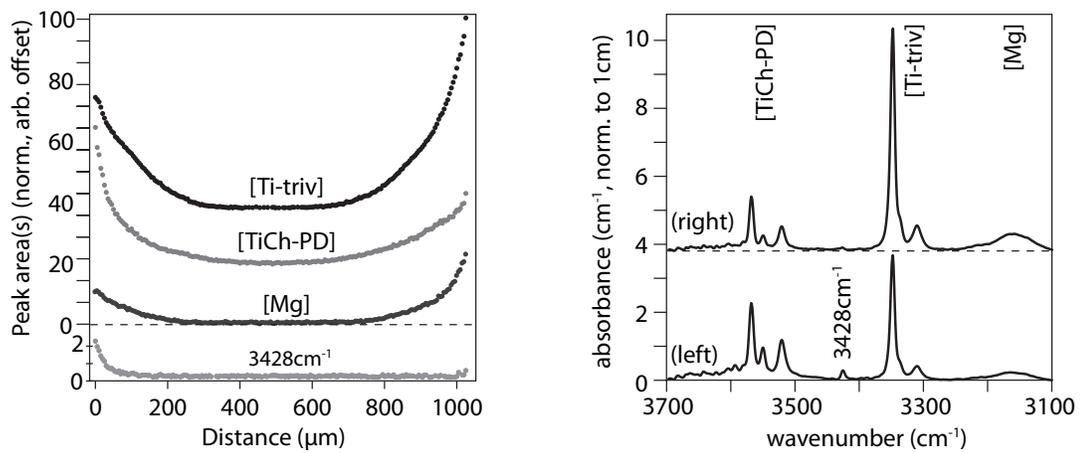


Figure 10

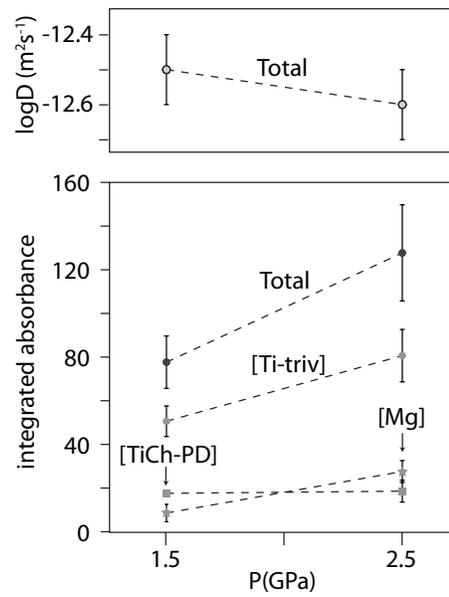


Figure 11

