Titatnium-Hydroxyl Defect-controlled Rheology of the Earth's Upper Mantle.

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Abstract

Experiments were conducted with hydrous olivine to investigate the defect responsible for the influence of water (hydrogen structurally incorporated as hydroxyl) on the olivine rheology. Solution-gelation derived Fo₉₀ olivine doped with nominally 0.04 - 0.1 wt.% TiO₂ was first hot-pressed and then deformed in platinum capsules at 300 MPa confining pressure and temperatures from 1200 - 1350°C. The water content was not buffered so that deformation occurred at water-undersaturated conditions. Due to the enhanced grain growth under hydrous conditions, the samples were at least a factor of three more coarse-grained than their dry counterparts and deformed in powerlaw creep at differential stresses as low as a few tens of MPa. Since all experiments were conducted at the same confining pressure, the essentially linear relationship between strain rate and water content was for the first time determined independently of an activation volume. Infrared spectra are dominated by absorption bands at 3572 and 3525 cm⁻¹. These bands also predominate in

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infrared spectra of natural olivine, and can only be reproduced experimentally in the presence of titanium. In contrast to the previous interpretation of the hydrous rheology in terms of intrinsic point defects, the experiments show that extrinsic defects (impurities) in natural olivine play the dominant role for water weakening at the water contents expected for most of the upper mantle.

Keywords: upper mantle, deformation, olivine, water, defects, FTIR spectroscopy

1. Introduction

It is well established that olivine deformed in the presence of water is weaker than when deformed under dry conditions (Avé Lallemant and Carter, 1970; Chopra and Paterson, 1984; Mackwell et al., 1985; Karato et al., 1986; Mei and Kohlstedt, 2000a,b). These studies confirmed a relationship between the presence of water and strength, but because experiments were always carried out under water-saturated conditions the relationship between water fugacity and strength were not determined independently of confining pressures (Hirth and Kohlstedt, 2003; Karato and Jung, 2003).

Less clear is the point defect mechanism for weakening due to water. Fits to experiments at a range of pressures yielded a relationship between strain rate and water fugacity (fH_2O) with an exponent r as $\dot{\epsilon} \propto fH_2O^r$. Models of point defects were then examined to obtain the same exponent through a combination of the dominant defect for charge neutrality and diffusive accommodation of strain (Karato, 1989a; Mei and Kohlstedt, 2000a,b). The hydrous defects thus inferred can not be readily reconciled with infrared

17 absorption spectra from experiments aimed at correlating absorption bands
18 with particular defects (Matveev et al., 2001; Lemaire et al., 2004; Berry
19 et al., 2005). The defect models for deformation considered only intrinsic de-
20 fects (vacancy and interstitial O, Mg, Fe^{2+} , Si, Fe^{3+} on octahedral and tetra-
21 hedral sites, and electrons, Kohlstedt and Mackwell (1998)). By contrast,
22 natural olivine contains a range of impurities with abundances in the ppm
23 range (extrinsic defects, de Hoog et al. (2010); Foley et al. (2013)). Previous
24 experiments showed that titanium is required to experimentally reproduce
25 the infrared spectra typical of natural samples (Berry et al., 2005). *Ab initio*
26 modelling indicated that the associated hydrous defect is the most stable
27 defect, potentially affecting the strength of olivine (Walker et al., 2007).

28 The experiments described in the following were carried out with Ti-
29 doped olivine to investigate the role of this impurity on the rheology under
30 hydrous conditions. The use of Pt capsules and $\text{Ni}_{70}\text{Fe}_{30}$ foils permitted wa-
31 ter retention at a range of water contents at fixed confining pressure. The
32 experiments were conducted at water-undersaturated conditions correspond-
33 ing to those for most of the upper mantle. Infrared spectra were used to
34 determine the water content and identify the hydrous defect associated with
35 the observed water weakening.

36 2. Sample Materials and Experimental Setup

37 The starting materials for the experiments were prepared by a solution-
38 gelation process, resulting in fine-grained, chemically pure and homogeneous
39 precursors (Faul and Jackson, 2007). For this study, Ti was added as tetra-
40 ethoxy orthotitanate (TEOT, Berry et al. (2007b)). The amount of Si in

41 the gel was in excess of stoichiometric olivine (Fo_{90}) composition to ensure
 42 Si saturation (Figure 1). After drying of the solution, the raw powders were
 43 reacted at 875°C and repeatedly fired at 1200°C and an $f\text{O}_2$ near the CCO
 44 buffer for more than 12 hours. The powders were cold pressed into pellets
 45 that were again fired at an $f\text{O}_2$ near the CCO buffer and kept in a drying
 46 oven until wrapping in $\sim 70\ \mu\text{m}$ thick $\text{Ni}_{70}\text{Fe}_{30}$ foil (with nominally either 0.04
 47 or 0.1 wt.% TiO_2 added) or encapsulation in laser-welded Pt capsules (0.04
 48 wt.% TiO_2 added, with a foil thickness of $180\ \mu\text{m}$ and $250\ \mu\text{m}$ for hotpressing
 49 and deformation experiments, respectively). Table 1 provides a summary
 50 of experimental conditions and compositions. Each wrapped/encapsulated
 51 sample was inserted in a mild steel jacket and hot-pressed for 24 h at the same
 52 temperature as the subsequent deformation experiment. The temperature
 53 uncertainty is estimated as $\pm 10^\circ\text{C}$ from regular furnace calibrations. All
 54 experiments were carried out at a confining pressure of 300 MPa.

55 After hot-pressing, the jacket was dissolved in acid, the Pt capsule peeled
 56 off and a $\sim 1\ \text{mm}$ thick slice was sectioned about 1.5 mm from the top
 57 end of the sample for microstructural examination and Fourier transform in-
 58 frared (FTIR) spectroscopy. Each fully dense sample was precision ground
 59 to a cylinder with a diameter of 11.5 mm and a lengths near 25 mm before
 60 being refired at CCO and 1200°C for 12 h prior to re-encapsulation for de-
 61 formation. The deformation experiments were carried out in a gas medium
 62 (Paterson) apparatus under triaxial compression in a pre-programmed se-
 63 quence of constant load segments, with load increasing after each segment.
 64 The load (force) was measured internally, displacements externally. Further
 65 details on the apparatus calibration and deformation procedures are given in

Table 1: **Summary of Experiments**

sample	capsule/ wrapper	T, °C	d^a , μm	water		titanium			stress MPa	strain, % ^f
				structural		molecular ppm H/Si ^b	ppm	wt.		
				ppm H/Si ^b	ppm H ₂ O ^c			ppm ^e		
6652	Ni ₇₀ Fe ₃₀	1278	23.8	100(38)	6	0	1940	635	18 - 220	9
6656	Ni ₇₀ Fe ₃₀	1200	29.8	10(6)	0.6	0	1940	635	114 - 320	16
6713	Ni ₇₀ Fe ₃₀	1300	6.7	0	0	0	660	216	20 - 75	2.5
6714	Ni ₇₀ Fe ₃₀	1200	6.5	0	0	0	660	216	75 - 100	2.1
6774	Pt	1200	20.0	490(280)	30	86(62)	798	261	37 - 241	13
6767	Pt	1200	15.9	724(140)	45	179(76)	798	261	65 - 213	37
6795	Pt	1250	40.0	542(370)	33	181(180)	866	283	30 - 232	9
6754	Pt	1300	70.2	821(280)	50	119(110)	698	228	23 - 72	21
6803	Pt	1350	22.4	639(110)	39	564(140)	866	283	5 - 74	27

^a grain size determined from EBSD maps.

^b equivalent to the atomic ratio H/10⁶Si. Average values from the radial transects of each sample. Values in parenthesis represent one standard deviation of the transects (see Appendix A).

^c ppm by weight.

^d equivalent to the atomic ratio Ti/10⁶Si

^e ppm Ti by weight.

^f total strain at the end of the experiment.

Figure 1: **Representative** scanning electron microscope backscattered-electron image of the microstructure after hotpressing (**prior to deformation**). The grayscale variation of olivine crystals is due to orientation contrast. Darker patches predominantly on olivine grain boundaries and corners are orthopyroxene grains. Small orthopyroxene grains are also incorporated into olivine during growth from an estimated grain size of $1\ \mu\text{m}$ prior to hotpressing. Cracks originate during cooling due to the thermal expansion anisotropy of olivine. Small pores inside olivine grains stand out due to their bright rim.

66 Faul and Jackson (2007). After deformation a horizontal slice about 1mm
 67 thick and 1.5 mm from the top or bottom end of each sample was prepared
 68 for microstructural and analytical examination.

69 The total strain for samples 6652 and 6656 with 0.1 wt.% Ti and deformed
 70 in $\text{Ni}_{70}\text{Fe}_{30}$ foils after the first ‘staircase’ of constant load was relatively small.
 71 Therefore, the load was reduced to zero and a second pass was programmed.
 72 This second pass provides a measure of the reproducibility of the strain rates.
 73 Similarly, 6795 with modest total strain was deformed again as 6803 after
 74 precision grinding to 10 mm diameter and 20 mm length, firing at 1200°C

75 at CCO conditions and re-encapsulation in Pt. Samples that were deformed
76 to relatively high strains (6767 and 6803) began to flow around the pistons
77 at both ends. In some instances canting was observed as a consequence of
78 deformation.

79 3. Analytical Methods

80 The samples were examined optically, by scanning electron microscopy
81 (SEM), electron back-scatter diffraction (EBSD), electron probe micro-analysis
82 (EPMA), laser ablation inductively coupled mass spectrometry (LA-ICPMS)
83 and FTIR spectroscopy. Imaging and EBSD mapping were performed using
84 a Zeiss Ultra Plus field emission scanning electron microscope at the Center
85 for Advanced Microscopy at ANU. The EBSD maps were collected with an
86 Oxford Instruments camera and HKL software from carbon coated samples
87 at 20 kV acceleration voltage and 5 nA beam current. The maps consist of
88 400 x 400 or 450 x 450 points with indexing rates usually near 80%. The
89 maps were processed with MTEX software. The grain sizes were determined
90 from the EBSD maps as the equivalent diameter of a circle with the same
91 area of each grain in the map. A sectioning correction factor of $4/\pi$ was
92 applied to obtain the mean diameters in Table 1.

93 Microprobe analyses were performed using the CAMECA SX100 micro-
94 probe at RSES, ANU on selected samples to determine the Mg# (the molar
95 ratio $100 \text{ Mg}^{2+}/(\text{Mg}^{2+} + \text{Fe}^{2+})$). LA-ICPMS was performed at RSES ANU
96 with an Excimer laser and a single collector mass spectrometer (Agilent
97 7700) with a spot size of 70 μm to determine the Ti contents in olivine given
98 in Table 1. We also analysed a NIST 610 glass as a standard.

99 FTIR spectroscopy and the determination of the water content are de-
100 tailed in Appendix A. Briefly, we measured the absorbance on 400 micron
101 thick sections to enable measurements even at low water contents. Molecular
102 water and hydroxyl contents were determined separately from the spectra.
103 For the hydroxyl content we used the site-specific absorption coefficient from
104 Kovacs et al. (2010), which is similar to the coefficient of Bell et al. (2003).
105 The water content given in Table 1 is averaged from 25 - 30 measurements
106 on radial traverses.

107 4. Results

108 4.1. Composition, Microstructure and Water Content

109 After hotpressing, the samples are characterised by a near ideal ‘foam’
110 microstructure (Figure 2a) with equant crystalline grains and a relatively
111 narrow grain size distribution (Figure 3, left). Orthopyroxene, derived from
112 the excess silica in the gel as well as from grinding of the powders in agate
113 mortars, is relatively homogeneously distributed as small grains located fre-
114 quently at olivine grain corners (Figure 1). Grain growth rates for water-
115 bearing samples are significantly faster than for dry samples (Table 1, Karato
116 (1989b)), with growth rates modulated by the orthopyroxene grains. Grains
117 with non-uniform orientation (coloured in Figure 2a) indicate coalescence of
118 neighbours.

119 Samples deformed to relatively low strains experienced some grain growth
120 during deformation, with grain size distributions that are similar to those af-
121 ter hotpressing (compare 6793 and 6795). Deformation to strains approach-
122 ing or exceeding 30% leads to extensive recrystallisation with significant grain

Figure 2: EBSD maps of a hotpressed (a) and a deformed sample (b). Black lines show grain boundaries defined by misorientations of neighbouring pixels $> 10^\circ$. The colors represent grain internal misorientations relative to the mean orientation of each crystalline grain. White patches are not indexed areas and orthopyroxene grains. The hotpressed sample 6760 (a) has near ideal ‘foam microstructure’ with relatively equant grains and no grain internal deformation (gray). After deformation of this sample (b) the microstructure is characterised by extensive recrystallisation with mobile grain boundaries and strong grain internal deformation. The sample was deformed to a total strain of 37% (6767).

123 internal strain, complex grain shapes and interpenetrating grains (Figure 2b)
 124 and significantly broader grain size distributions (Figure 3).

125 Microprobe analyses of selected samples showed a uniform composition
 126 of the olivine with an average Mg# of 89.7 ± 0.5 . The Ti content varies
 127 somewhat between different batches of the gel due to the difficulty in precisely
 128 adding small quantities of TEOT (one sample per batch was analysed by
 129 laser-ablation ICPMS). With two H per Ti atom expected for the titanium
 130 clinohumite-type point defect, comparison of the H and Ti contents in ppm/Si

Figure 3: Distributions of grain sizes **normalized by the mean** grain size of samples after hot-pressing and after deformation. The hotpressed samples have narrow grain size distributions, while distributions of the samples deformed to high strain (e.g. 6767) are much broader, indicating extensive recrystallisation. At 9% strain (6795) recrystallization is only incipient, and grain growth is still occurring.

131 (Table 1) shows that typically less than half of the Ti is associated with
 132 protonated defects in the deformed materials. Water contents of hotpressed
 133 samples are higher (up to 1430 ppm H/Si or 88 wt. ppm H₂O), but remain
 134 at or below saturation of the Ti sites. The lower water content of deformed
 135 samples confirms that they are water-undersaturated during deformation.

136 FTIR spectra of samples doped with nominally 0.04 wt.% TiO₂ (the ac-
 137 tual concentrations are given in Table 1) and hotpressed and deformed in
 138 Pt, show two distinct absorption bands at 3572 and 3525 cm⁻¹, indicating
 139 the presence of structurally bound hydrogen (hydroxyl). In addition a broad
 140 absorption region centred on 3450 cm⁻¹ is observed in essentially all samples
 141 (Figure 4). This broad absorption region corresponds to molecular water,
 142 likely contained in small pores (Figure 1). Samples with 0.04 wt.% TiO₂ hot-

143 pressed and deformed in $\text{Ni}_{70}\text{Fe}_{30}$ foils are completely dry (e.g. 6713), while
 144 samples with a higher Ti content (nominally 0.1 wt.% TiO_2) in $\text{Ni}_{70}\text{Fe}_{30}$ foils
 145 retain small amounts of water after deformation (e.g. 6652).

Figure 4: **Representative** FTIR spectra of hotpressed (a) and deformed samples (b). The unpolarised absorption spectra were obtained from sections that are $\sim 400 \mu\text{m}$ thick. All samples show the absorption bands characteristic of the titanium-clinohumite like point defect (vertical lines at 3572 and 3525 cm^{-1}). The spectra were collected approximately 1.5 mm from the outer edge of the samples, except for $\text{Ni}_{70}\text{Fe}_{30}$ foil-wrapped 6652 (interior). In the post-deformation Pt encapsulated samples the outer regions typically have higher water contents compared to the interiors, while hotpressed samples have more uniform water contents. The water contents given in Table 1 are volumetric averages of concentric cylindrical volumes for which the water contents were determined from transects on the horizontal slices consisting of 25 - 30 spectra from center to rim of each sample (see Appendix A). The spectrum labelled ‘pellet’ shows adsorbed water in cold pressed pellets after firing prior to encapsulation in Pt for hotpressing. The spectrum from 6713 shows an example from a $\text{Ni}_{70}\text{Fe}_{30}$ foil wrapped sample that is dry.

146 Fe-bearing samples in contact with Pt are oxidised by the loss of Fe to

147 the capsule (e.g. Jaques and Green (1980) and references therein). The Fe
 148 content in olivine decreases from Fo₉₀ in the interior to about Fo₉₈ adjacent to
 149 the Pt capsule over a radial distance of about 100 μm , with a corresponding
 150 increase of the fO₂ from iron-wüstite (IW) +2 in the interior to IW+5 at the
 151 capsule. The interior of the samples is therefore to some extent self buffering.
 152 The fO₂ of Ni₇₀Fe₃₀ foil-wrapped samples is slightly above IW. We infer that
 153 the relatively high fO₂ and correspondingly high fH₂O and low fH₂ (Mackwell
 154 and Kohlstedt, 1990) adjacent to Pt capsules is necessary to retain hydrogen
 155 over the 8 - 24 h duration of the experiments without buffer. Hydrogen
 156 retention was not observed in tests with Ni capsules with 0.04 wt.% TiO₂.
 157 Further details of the fO₂ determination in sample interiors using dispersed
 158 Pt particles following the approach of Rubie et al. (1993) will be published
 159 separately.

160 4.2. Rheology

161 Rheological data are generally fitted to an empirical flow law of the form:

$$\dot{\epsilon} = A \sigma^n d^{-p} C_{OH}^r \exp^{-(E+PV)/RT}, \quad (1)$$

162 where $\dot{\epsilon}$ is the axial strain rate, σ the differential stress, d the grain size, A
 163 a constant, E the activation energy for creep, P pressure, T the (absolute)
 164 temperature, R the gas constant, n the stress exponent and p the grain size
 165 exponent (Mei and Kohlstedt, 2000b; Karato and Jung, 2003; Hirth and
 166 Kohlstedt, 2003). C_{OH} is the water content in units of ppm H/Si (i.e. H/10⁶
 167 Si) with exponent r . Values for the activation volume V were obtained
 168 from the literature (Hirth and Kohlstedt, 2003; Karato and Jung, 2003).
 169 Structurally bound hydrogen (hydroxyl) contents in our experiments after

170 deformation range from 10 to 820 ppm H/Si (~ 0.6 to 50 weight ppm water),
171 with the lowest water contents observed for samples deformed in $\text{Ni}_{70}\text{Fe}_{30}$ foils
172 (Table 1). With one exception, molecular water contents are significantly
173 lower.

174 Plots of strain rate as a function of stress reveal two different deforma-
175 tional regimes (Figure 5). A shallow slope at low stresses (most clearly seen
176 in samples 6652 and 6803 in Figure 5b) indicates diffusion creep with a linear
177 stress and cubic grain size dependence in Equation 1. As a consequence of
178 the coarse grain size of the starting aggregates, most of the data are con-
179 sistent with a steeper slope and a stress exponent $n = 3.5$, a value that is
180 characteristic of grain size-independent dislocation creep for olivine (Chopra
181 and Paterson, 1984; Hirth and Kohlstedt, 2003). The most coarse-grained
182 samples (mean grain sizes 40 - 70 μm) deform by dislocation creep at a stress
183 below 50 MPa. This transition in the dominant deformation mechanism oc-
184 curs at higher stresses for decreasing grain size. No grain size sensitivity is
185 observed in this powerlaw creep regime for samples with grain sizes $> 15 \mu\text{m}$.

186 For comparison with the experimental data, strain rates calculated with
187 published flow laws (with parameters from Hirth and Kohlstedt (2003), those
188 of Karato and Jung (2003) are similar) are shown by the solid lines in Figure
189 5. For this calculation the hydroxyl contents in Table 1 were used (see Sec-
190 tion 5.1). The pre-exponential constant for diffusion creep was increased to
191 be consistent with the current results. All other parameters, including the
192 activation energies and water content exponents, are the same as those ob-
193 tained previously from water-saturated experiments at a range of confining
194 pressures (Karato and Jung, 2003; Hirth and Kohlstedt, 2003).

Figure 5: Rheology of hydrous, Ti-doped olivine as a function of hydroxyl content. **a** 1200°C data, and **b** data from 1250 - 1350°C experiments. Symbols represent rheological data from this study (Supplementary Tables 3 - 7). Solid lines, with the same colour as the associated data points were calculated with the rheological parameters (Table 2, Hirth and Kohlstedt (2003)) for the water contents indicated in the legend for each sample in ppm H/Si. For reference, dry dislocation creep rheologies are indicated by solid black (Chopra and Paterson, 1984), and dashed lines (Hirth and Kohlstedt, 2003). The shallower slopes at low stress for some of the samples with grain sizes near 20 μm (e.g. 6652) indicate deformation by diffusion creep. The coarse-grained sample 6754 deforms by dislocation creep below 50 MPa. The noticeable deviation from the flow law (lines) of samples 6656 and 6795 likely reflects uncertainties in their water contents.

195 Samples doped with ~ 0.04 wt.% TiO_2 hotpressed and deformed in $\text{Ni}_{70}\text{Fe}_{30}$
196 foils do not contain detectable water (Figure 4, 6713). Consistent with the
197 absence of detectable water they remained fine-grained ($< 7 \mu\text{m}$, Table 1).
198 Their diffusion creep rheology is somewhat weaker than the rheology of un-
199 doped Fo_{90} solgel (Faul and Jackson, 2007), and can be modelled with the
200 parameters in Table 2 with 5 ppm H/Si (Figure 6). Ti by itself thus con-
201 tributes only very modestly to the enhanced strain rates of the experiments

Figure 6: Diffusion creep rheology of dry Ti-doped olivine. The samples are weaker than the undoped Fo_{90} rheology of Faul and Jackson (2007) (FJ07, solid lines), but stronger than the dry, nominally melt-free rheology of Hirth and Kohlstedt (1995, 2003) (HK03, long dashed shown for 1300° only) . The strength of the dry, Ti-doped (0.04 wt.% TiO_2) samples is adequately described by the parameters in Table 2 with a water content of 5 ppm H/Si (dashed).

described here.

5. Discussion

5.1. Possible Effect of Molecular Water

Experiments on silicon self-diffusion in olivine showed high diffusivities under dry conditions and only minor enhancements under water-undersaturated conditions (Fei et al., 2012, 2013), leading to the proposal that water has only a minor effect on the rheology of olivine. Previous deformation experiments on polycrystalline aggregates conducted with the aim of determining the effect of water on rheology were carried out with a buffer assembly to ensure that the samples remained water saturated (Mei and Kohlstedt, 2000a; Jung

Table 2: **Flow Law Parameters (Equation 1)**

	A	n	p	r	E	V
	$\text{MPa}^{-n} \text{ s}^{-1} \mu\text{m}^p \text{ C}_{\text{H}_2\text{O}}^{-r}$				kJ/mol	$10^{-6} \text{ m}^3/\text{mol}$
diffusion	4×10^5	1	3	1	335	4
dislocation	90	3.5	0	1.2	480	11

Parameters (grain size in μm , stress in MPa and water contents in ppm H/Si) are from Hirth and Kohlstedt (2003), except the pre-exponential constant for diffusion creep, which has been adjusted to fit our data. The parameters of Karato and Jung (2003) are overall similar, but with a somewhat lower activation energy. Pre-exponential constant A in SI units: $A_{diff} = 4 \times 10^{-19} \text{ Pa s}^{-1} \text{ m}^3 \text{ C}_{\text{H}_2\text{O}}^{-1}$, $A_{disloc} = 9 \times 10^{-20} \text{ Pa}^{-3.5} \text{ s}^{-1} \text{ C}_{\text{H}_2\text{O}}^{-1.2}$, for stress in Pa and grainsize in m. $r = 1$ and E 460 kJ/mol (A unchanged) for dislocation creep are also compatible with our data (Figure 7).

212 and Karato, 2001). FTIR spectra of these deformed polycrystalline samples
213 are dominated by molecular water, which was presumed to reside in pores
214 and at grain boundaries (Mei and Kohlstedt, 2000a). This free water was
215 suggested to have contributed to the substantial reduction in creep strength
216 compared to dry aggregates (Fei et al., 2013). Molecular water is absent at
217 the water-undersaturated conditions of most of the Earth’s upper mantle,
218 raising the question of whether previous hydrous deformation experiments
219 may have overestimated the effect of water on the rheology. The diffusion
220 experiments showing little influence of water on diffusivity (Fei et al., 2013)
221 were conducted with Ti-free synthetic forsterite (Fei et al., 2012), while ear-
222 lier hydrous diffusion experiments finding a significant effect of water on
223 diffusivity were conducted with Ti-bearing San Carlos olivine (Costa and
224 Chakraborty, 2008).

225 Determining hydroxyl and molecular water contents separately enables

Figure 7: Dislocation creep data for each sample recalculated for a common temperature of 1200°C and a common stress of 150 MPa as a function of water content (Table 1). The scatter in strain rates after normalisation gives an indication of the uncertainty in the rheological data. Standard deviations of the 25 - 30 analyses per sample are shown as uncertainties in water contents (thin black lines). **a)** Molecular water. A fit to the data of the present study requires $r \sim 0.7$ and constant $A \sim 7000$. However, a flow law with these values does not intersect the dry dislocation creep rheology (CP84, Chopra and Paterson (1984), HK03, Hirth and Kohlstedt (2003) (black symbols). **b)** Structurally bound hydrogen (hydroxyl). The data is well described by the parameters given in Table 2 ($r = 1.2$) intersecting the dry rheology of Chopra and Paterson (1984) at 5 ppm H/Si. The dashed line indicates $r = 1$, $E = 460$ kJ/mol, intersecting the dry rheology at 1 ppm H/Si. Grey dots at 130 ppm H/Si are data from Mei and Kohlstedt (2000a), black dots from Tasaka et al. (2015) (see Section 5.4). Inset in b) shows an FTIR spectrum from sample 6803 that contains contributions from hydroxyl (green, absorption bands at 3572 and 3525 cm^{-1} , black vertical lines indicate the limits of integration) and molecular water (gray).

226 examination of the measured strain rates as a function of these two com-
 227 ponents (Figure 7). For this comparison the dislocation creep data were

228 recalculated for a common temperature of 1200°C and differential stress of
 229 150 MPa with Equation 1 and the parameters in Table 2. Hirth and Kohlstedt
 230 (2003) infer that the transition from a ‘wet’ rheology to a ‘dry’ rheology
 231 occurs at a water content of 50 ppm H/Si (i.e. 50 H/10⁶Si or ~ 3 weight ppm
 232 H₂O) based on their dry rheology. The somewhat lower strain rates observed
 233 by Chopra and Paterson (1984) for dry olivine imply a wet to dry transition
 234 at ~ 5 ppm H/Si. In diffusion creep this value for the wet to dry transition
 235 is supported by the rheology of dry, Ti-doped samples (Figure 6). Hirth and
 236 Kohlstedt (2003) do not distinguish between molecular water and hydroxyl,
 237 so both rheologies are plotted at their respective inferred water content at
 238 the wet to dry transition.

239 Samples deformed in Ni₇₀Fe₃₀ foils contain no detectable molecular water,
 240 only small amounts of hydroxyl. If molecular water controlled the rheology,
 241 these samples should have strain rates consistent with the published dry
 242 rheologies (Chopra and Paterson, 1984; Hirth and Kohlstedt, 2003) (Figure
 243 7a). A fit to the molecular water content of this study would have indeed a
 244 smaller water concentration exponent $r \sim 0.7$ relative to published fits (Hirth
 245 and Kohlstedt, 2003; Karato and Jung, 2003), but would not intersect the
 246 published dry rheologies. It is thus unlikely that the rheology of olivine is
 247 controlled by the molecular water content.

248 When plotted as a function of hydroxyl content, the experimental strain
 249 rates fall with some scatter on the strain rates calculated with Equation 1
 250 based on published parameters for dislocation creep (Table 2, Figure 7b).
 251 This flow law intersects the dry rheology of Chopra and Paterson (1984)
 252 at a hydroxyl content of ~ 5 ppm H/Si, indicating the transition to a dry

253 rheology at this low water content. Alternatively if the wet to dry transition
254 is assumed to occur at a hydroxyl content of 1 ppm H/Si the exponent r
255 would have a value of one, together with a somewhat lower activation energy
256 (460 kJ/mol).

257 The powerlaw rheology, lack of grain size sensitivity, and the recrystalli-
258 sation observable in experiments with high strains (Figure 2b) all point to a
259 grain internal (dislocation) mechanism for deformation. This grain internal
260 mechanism is not sensitive to the water content of grain boundaries. Figure
261 7b shows that the hydroxyl content in the Ti-related absorption bands can
262 explain the observed enhancement of the strain rates relative to dry condi-
263 tions, rather than molecular water (Fei et al., 2013).

264 5.2. *Structural Site for Hydrogen Incorporation in Olivine from IR spectra*

265 Infrared spectra of natural olivine show more than 50 absorption bands
266 between 3612 and 3160 cm^{-1} (e.g. Beran and Libowitzky (2006) and refer-
267 ences therein). These bands, due to absorption of infrared energy associated
268 with the stretching of OH bonds, indicate that hydrogen is incorporated
269 into the olivine crystal structure as a trace element at different defect sites
270 with corresponding absorption bands. Experiments attempting to reproduce
271 the natural spectra, and associate specific defects with individual absorp-
272 tion bands are complicated by the use of different starting materials, types
273 of capsules and buffering conditions, and pressures at which they were con-
274 ducted. In the following, different experiments and conditions are discussed
275 to highlight their systematics.

276 Infrared spectra of samples of experiments with both natural and syn-
277 thetic olivine exhibit differences attributed to silica activity (Matveev et al.,

278 2001; Lemaire et al., 2004; Berry et al., 2005). At high silica activity (or-
 279 thopyroxene buffered) bands are observed at wave numbers below 3400 cm^{-1} ,
 280 in particular the high silica activity band at 3160 cm^{-1} . At low silica activ-
 281 ity (magnesio-wüstite buffered) bands are observed between 3612 and 3430
 282 cm^{-1} , with the most prominent bands at 3612 , 3579 and 3567 cm^{-1} (Lemaire
 283 et al., 2004; Berry et al., 2005). The bands above wave numbers of 3400 cm^{-1}
 284 (group I bands of Bai and Kohlstedt (1993)) are therefore associated with
 285 tetrahedral (Si) site related defects, while the bands below 3400 cm^{-1} (group
 286 II bands of Bai and Kohlstedt (1993)) are associated with octahedral (M)
 287 site defects.

288 Doping synthetic forsterite with a range of trivalent cations results in ab-
 289 sorption bands between 3400 and 3300 cm^{-1} (Berry et al., 2007a). The exper-
 290 iments show correlations between the location of the most intense absorption
 291 band and the ionic radius of the trivalent cation, and the concentration of
 292 a cation and the absorbance. Hydrogen associated with Fe^{3+} produces the
 293 most intense absorption bands at 3350 and 3331 cm^{-1} (Berry et al., 2007a),
 294 explaining the strong $f\text{O}_2$ dependence observed for the group II bands by Bai
 295 and Kohlstedt (1993), and the absence of these bands for olivine at low $f\text{O}_2$,
 296 even at high silica activity. Consistent with this interpretation, the experi-
 297 ments on Fo_{90} olivine in Pt capsules exhibit bands between 3400 and 3300
 298 cm^{-1} (Matveev et al., 2001; Berry et al., 2005), while these bands are absent
 299 for Fo_{100} prepared under similar conditions (Lemaire et al., 2004; Berry et al.,
 300 2005).

301 The most ubiquitous, and frequently the only, bands observed in natural
 302 olivine from regions of the Earth's upper mantle that are far from water

303 saturation and unaffected by hydrothermal alteration, are those at 3572 and
 304 3525 cm^{-1} (Miller et al., 1987; Bell et al., 2003; Demouchy et al., 2006; Beran
 305 and Libowitzky, 2006; Peslier et al., 2010). These two bands are also the only
 306 ones observed in untreated San Carlos olivine (Mackwell et al., 1985; Bai and
 307 Kohlstedt, 1993; Berry et al., 2005). Spectra from experiments at 300 MPa
 308 confining pressure conducted with San Carlos olivine always include these
 309 two bands, among others (Mackwell et al., 1985; Mackwell and Kohlstedt,
 310 1990; Bai and Kohlstedt, 1992, 1993; Kohlstedt and Mackwell, 1998; Mei and
 311 Kohlstedt, 2000a; Mei et al., 2002; Zhao et al., 2004; Tasaka et al., 2015).

312 Experiments with natural and synthetic olivine show that the bands at
 313 3572 and 3525 cm^{-1} and their relative intensities can only be reproduced
 314 in either pure forsterite or Fo_{90} olivine if the samples contain Ti (Berry
 315 et al., 2005, 2007a; Padrón-Navarta et al., 2014). Because these bands occur
 316 at the same energies as two of the main bands of natural Ti-clinohumite,
 317 the defect is referred to as Ti-clinohumite-like point defect (see Berry et al.
 318 (2007b) and references therein). San Carlos olivine contains 10 - 25 atom
 319 ppm Ti (equivalently 18 - 46 ppm Ti/Si, de Hoog et al. (2010), see below)
 320 and consequently exhibits the corresponding absorption bands under hydrous
 321 conditions. Experimental observations indicate that the Ti-related bands are
 322 present regardless of silica activity (Bai and Kohlstedt, 1993; Berry et al.,
 323 2005).

324 Absorption frequencies for hydrated defects calculated from first princi-
 325 ples with quantum chemical methods are consistent with the experimental
 326 observations (e.g. Walker et al. (2007); Balan et al. (2011); Umemoto et al.
 327 (2011)). Models of hydrated Si vacancies result in calculated absorption

bands at frequencies $> 3450 \text{ cm}^{-1}$, while hydrated M-site vacancies result in bands at frequencies $< 3300 \text{ cm}^{-1}$. Walker et al. (2007) and Balan et al. (2011) confirm the Ti-defect as energetically the most favourable hydrous defect, with location of the bands and their polarisation, as well as site-specific absorbance consistent with observations.

In summary, the following hydrous defect types in olivine can be distinguished: tetrahedral- (Si), Ti-, octahedral- (Mg), and trivalent- (M^{3+}) related. This distinction was confirmed by the observation of different rates of change of band height and hence diffusivities for the different defects in diffusion experiments (Padrón-Navarta et al., 2014), as well as natural samples (Peslier et al., 2015).

In higher pressure experiments ($> 5 \text{ GPa}$) the most intense bands occur at 3612 and 3567 cm^{-1} (Kohlstedt et al., 1996; Mosenfelder et al., 2006), with a number of other peaks merging and producing broad absorbance in this region. The height of the most intense bands is several times greater than those in the 300 MPa experiments, indicating a higher solubility. The Ti-related bands, with absorbance limited by the amount of Ti in the San Carlos olivine used in the experiments, are subsumed into this broader absorption region.

A potential complication with the experimental assemblies of Kohlstedt et al. (1996) is that while they included orthopyroxene, the presence of pure forsterite in contact with Fo_{90} San Carlos olivine indicates that chemical equilibrium was not attained. As Si is slower to diffuse than Mg, and orthopyroxene was further away from the San Carlos olivine single crystal than the forsterite, it is possible that the Si-activity was not buffered. However,

thermodynamic calculations suggest that at high fH₂O hydrated defects associated with Si will become increasingly important even with Si-buffering (Walker et al., 2007).

5.3. Defect Models for Hydrous Deformation

The creep rate during deformation is limited by the diffusivity of the slowest ionic species diffusing along its fastest path. For diffusion by a vacancy mechanism the diffusivity of an ion depends on the concentration of this vacancy. The concentrations of point defects in turn are constrained by charge neutrality, which therefore needs to be considered in models of deformation. Intrinsic point defects in olivine include tetrahedral (Si), octahedral (M) and oxygen vacancies and interstitials (see also previous section).

Based on a range of experimental observations, under anhydrous conditions, the dominant charge neutrality condition for olivine is inferred to consist of Fe³⁺ on metal sites charge-balanced by metal site vacancies (Nakamura and Schmalzried, 1983; Karato, 1989a; Mei and Kohlstedt, 2000a; Kohlstedt, 2006), at least under oxidising conditions (Kohlstedt and Mackwell, 1998). In Kröger-Vink notation this is expressed as $[M_M^\bullet] = 2[V_M'']$, where square brackets indicate concentration, $M_M^\bullet$ a metal ion with a single excess positive charge on a metal site (i.e. Fe³⁺), and V_M'' a metal site vacancy, implying two negative charges. Deformation of olivine is rate-limited by Si as the slowest diffusing ionic species (Jaoul et al., 1981; Hirth and Kohlstedt, 2003; Kohlstedt, 2006; Dohmen and Milke, 2010).

In the presence of water, protons (denoted by p[•]) affect defect concentrations and charge neutrality. The observation of enhanced strain rates implies that the concentration of Si vacancies is increased in order to increase Si dif-

378 fusivity. The law of mass action can be used to show that the concentration
 379 of each point defect is proportional to the water fugacity to an exponent r :
 380 $[] \propto (fH_2O)^r$ (Karato, 1989a; Mei and Kohlstedt, 2000a). Water fugacity
 381 can be converted to concentration by considering an activation enthalpy for
 382 the incorporation of hydroxyl (Kohlstedt et al., 1996; Keppler and Bolfan-
 383 Casanova, 2006).

384 With this approach, the dominant defects under hydrous conditions can
 385 then be obtained by comparing the experimentally determined exponent r in
 386 Equation 1, with that predicted by the combination of dominant defect for
 387 charge neutrality and involvement of tetrahedral site defects from the law of
 388 mass action (see e.g. Kohlstedt (2006); Karato (2008)). The combination of
 389 doubly protonated Si vacancies, $(2H)''_{Si}$ with the charge neutrality condition
 390 $[p^\bullet] = [H'_M]$ yields a water fugacity exponent of one, which is near the exper-
 391 imentally determined value of 1.2 (Kohlstedt, 2006). However, based on the
 392 observations presented in the previous section, this combination of defects
 393 also implies that the FTIR spectra should exhibit both tetrahedral (group
 394 I) and octahedral (group II) bands, which is not always the case (Bai and
 395 Kohlstedt, 1992, 1993; Kohlstedt and Mackwell, 1998; Girard et al., 2013),
 396 and not observed in this study. As an alternative model for $r \sim 1$ Karato
 397 and Jung (2003) consider positively charged jogs and silicon interstitials.

398 The above model originates with experiments conducted on iron bear-
 399 ing olivine at dry conditions using high purity oxides where fO_2 was varied
 400 (Nakamura and Schmalzried, 1983). Variation of fO_2 affects the Fe^{2+}/Fe^{3+}
 401 ratio, which lead to the conclusion that defects involving metal site vacancies
 402 are the dominant intrinsic defects. However, natural olivine contains a range

403 of impurities such as Ti, Al, and Na, with oxidation states independent of
 404 fO_2 within the olivine stability field. Concentrations of these impurities range
 405 from a few wt. ppm to several hundred wt. ppm (de Hoog et al. (2010); Fo-
 406 ley et al. (2013), see Section 6). By comparison, estimated concentrations of
 407 metal vacancies are of order of tens of ppm at anhydrous conditions (Naka-
 408 mura and Schmalzried, 1983; Kohlstedt, 2006)). The abundance of extrinsic
 409 defects is therefore comparable to that of the most abundant intrinsic defect
 410 (Dohmen and Chakraborty, 2007). The latter authors also pointed out the
 411 need to consider extrinsic defects in models of diffusion.

412 Titanium occurs as Ti^{4+} at mantle conditions, and X-ray absorption spec-
 413 troscopy combined with ab initio calculations show that it occupies the Si
 414 site in dry olivine. On hydration Ti is octahedrally coordinated with two
 415 hydrogens on an adjacent silicon vacancy (Berry et al., 2007b; Walker et al.,
 416 2007). Hydration of the component Mg_2TiO_4 can be written as follows:

417 In the presence of an enstatite buffer MgO will react further:

418 Creation of a hydrous Ti-defect therefore increases the concentration of
 419 Si vacancies without affecting pre-existing (intrinsic) point defect concentra-
 420 tions. The above relations also show that hydration can occur regardless of
 421 oxide buffering. Equation 2 yields a linear dependence of concentration of
 422 the defect on fH_2O (Keppler and Bolfan-Casanova, 2006), consistent with
 423 a power-law exponent r near unity in Equation 1 (Table 2). The IR spec-
 424 tra (Figure 4) show that at water-undersaturated and Si-buffered conditions

425 only Ti defects are hydrated, but not metal or Si vacancies without an adja-
 426 cent Ti, whose hydration evidently requires more energy (c.f. Walker et al.
 427 (2007)). While at higher pressures (and fH₂O at saturated conditions), other
 428 defect species dominate (Kohlstedt et al., 1996), at low pressure and at water-
 429 undersaturated conditions the Ti-clinohumite defect is the dominant defect
 430 and controls the effect of water on the olivine rheology. For the present
 431 experiments at fixed confining pressure and at water-undersaturated condi-
 432 tions, the directly measured water concentrations constrain the parameter r
 433 in Equation 1 (Figure 7b).

434 *5.4. Rheology of Hydrous San Carlos Olivine*

435 As described above, FTIR spectra of San Carlos olivine always contain the
 436 Ti-related absorption bands. Trace element analyses of San Carlos olivine
 437 yield up to 46 ppm Ti/Si (de Hoog et al., 2010), implying about 90 ppm
 438 H/Si at saturation of the Ti defect. However, olivine from San Carlos can
 439 have a range of Mg# (Zhao et al., 2004), while the Ti concentrations of
 440 clinopyroxene are variable (Frey and Prinz, 1978), suggesting that the Ti
 441 content in olivine may also vary. Since the spectra showing structurally
 442 incorporated hydrogen in the experiments of Mei and Kohlstedt (2000a,b)
 443 and Mei et al. (2002) were obtained from large single crystals embedded in
 444 a much more fine-grained matrix, the Ti content of the single crystals and
 445 matrix may also differ, particularly if matrix and single crystal have different
 446 Mg# (Tasaka et al., 2015). The actual Ti content of the experimental samples
 447 is not available.

448 Analysis of published infrared spectra (Bai and Kohlstedt, 1993; Mei and
 449 Kohlstedt, 2000a; Tasaka et al., 2015) with the procedure described in Ap-

450 pendix A yields an approximate water content of about 130 ppm H/Si as-
 451 sociated with the Ti-defect (c.f. inset in Figure 7) for these experiments.
 452 This water content does not include hydroxyl in group II bands or molecular
 453 water, and is broadly consistent with the water content inferred from the Ti
 454 content above.

Figure 8: Deformation data of hydrous San Carlos olivine at two temperatures. Dots represent data from Mei and Kohlstedt (2000b) (300 MPa data only), squares data from Tasaka et al. (2015) (Fo₉₀ compositions only). Each colour represents data from one experiment. Lines represent strain rates calculated from Equation 1 with the parameters in Table 2 and a water content of 130 ppm H/Si. The approximate grain sizes relevant for the diffusion creep portions are indicated next to the lines. At 4 μm deformation occurs predominantly in diffusion creep while at 25 μm deformation occurs predominantly in (grain size independent) dislocation creep. Grain sizes for the samples of Mei and Kohlstedt (2000b) range from 15 to 18 μm , the two more coarse-grained samples from Tasaka et al. (2015) have grain sizes of 8 and 25 μm but deform similarly.

455 Rheological data from Mei and Kohlstedt (2000a,b) and Tasaka et al.
 456 (2015) are shown in Figure 8, along with strain rates calculated with the

parameters from Table 2 and a water content of 130 ppm H/Si. As the figure shows, within the scatter of the data, the measured strain rates are consistent with those calculated based on the hydroxyl contents in the Ti-related defects in San Carlos olivine, explaining the consistency with our data.

5.5. *Experimental Uncertainties*

Uncertainties arise primarily from possible temperature gradients along the length of the samples, as well as radial and longitudinal heterogeneities in water contents. Uncertainties in grain sizes will affect the diffusion creep data, but this is more of a problem for the dry samples with their smaller grain size. Temperature uncertainties are minimized (but not eliminated) by calibration experiments at regular intervals, typically before and after deformation experiments, so that possible changes in the temperature profile of the furnace can be accounted for. As described in Appendix A the water content for each sample given in Table 1 is averaged from volume weighted radial profiles. This may be the largest source of uncertainty and scatter seen in Figures 5 and 7b.

6. **Application to the Upper Mantle**

The above discussion links water weakening of olivine to its Ti content. Before applying the experimentally determined rheology to the upper mantle, Ti contents in olivine from the upper mantle need to be considered. Ti contents in olivine vary from a few wt. ppm to ~ 300 wt. ppm Ti (de Hoog et al., 2010; Peslier et al., 2010; Foley et al., 2013), with analyses being obtained predominantly from cratonic xenoliths. For comparison, the low Ti experiments contain ~ 220 wt. ppm Ti (800 ppm Ti/Si, Table 1). Most

481 xenoliths have a Mg# significantly above that expected for fertile upper
482 mantle, indicating that the rocks were affected by melt extraction, which
483 also decreases the Ti content. Subsequent metasomatism can increase the
484 Ti content to well above pre-depletion levels (de Hoog et al., 2010; Foley
485 et al., 2013). The data from de Hoog et al. (2010) suggests that olivine from
486 garnet peridotite xenoliths on average contains more Ti relative to olivine
487 from spinel peridotites.

488 The mid-ocean ridge basalt source upper mantle composition DMM in-
489 cludes olivine with a Mg#89.5 containing 102 wt. ppm Ti (Workman and
490 Hart, 2005). For asthenospheric mantle, with two H per Ti, the maximum
491 water content in olivine associated with the Ti defect (but not the total water
492 storage capacity) is ~ 600 ppm H/Si or about 40 wt. ppm H₂O.

493 Based on water contents of erupted mid-ocean ridge basalts, their mantle
494 source was inferred to contain 50 - 200 wt. ppm H₂O (Michael, 1988; Tenner
495 et al., 2012). Accounting for partitioning between the solid phases of the
496 mantle, before the onset of melting the water content of olivine was estimated
497 at 800 - 1000 ppm H/Si (Hirth and Kohlstedt, 1996), similar to the maximum
498 water content in the present experiments. More recent determinations of
499 the partition coefficient between olivine and pyroxene yielded estimates for
500 olivine water contents as low as 360 ppm H/Si at 70 km depth (Tenner et al.,
501 2012), which is below saturation of the Ti defect for the DMM composition.
502 The Ti defect can therefore accomodate most or all of the water content
503 predicted for olivine in the asthenosphere. The experiments presented here
504 show that at water-undersaturated conditions this defect is the most stable
505 hydrous defect and therefore the first to be hydrated.

506 Viscosities calculated with the parameters in Table 2 are shown in Figure
507 9 contoured by water content at constant shear stress and grain size. As
508 for seismic velocities (Faul and Jackson, 2005) the viscosity minimum occurs
509 where the conductive geotherm joins the adiabat. Below the minimum, the
510 rate of the viscosity increase with depth depends on the activation volume.
511 For this combination of grain size (10 mm) and stress (0.3 MPa), dislocation
512 creep dominates in the entire upper mantle for both wet and dry rheologies
513 in the oceanic case.

514 Assuming water is the only variable affecting the rheology in addition to
515 pressure and temperature, minimum viscosities $< 10^{19}$ Pa s as inferred for
516 example for the Western United States (Bills et al., 2007) or Iceland (Flem-
517 ing et al., 2007) require water contents of > 300 ppm H/Si at a stress of 0.3
518 MPa (Podolefsky et al., 2004). Water contents of up to 80 wt. ppm (~ 1300
519 ppm H/Si) in olivine have been observed in high pressure cratonic xenoliths
520 (Peslier et al., 2010), although not all water is associated with Ti. Poten-
521 tially these high water contents have implications for the long term stability
522 of cratons. However, high seismic velocities extending to significant depth
523 and the absence of a pronounced low velocity zone imply low temperatures
524 throughout most of the upper mantle beneath cratons. With temperatures
525 obtained from forward modeling of seismic velocities (Faul and Jackson, 2005;
526 Jackson and Faul, 2010) cratonic viscosities remain high even at high water
527 contents (Figure 9). Calculated minimum viscosities in the upper mantle of
528 order 10^{21} Pa s are consistent with those inferred from geodetic observations
529 for Fennoscandia (Milne et al., 2001) and North America (Tamisea et al.,
530 2007).

Figure 9: Viscosity of the Earth’s upper mantle as a function of water content calculated with the parameters from Table 2. Temperature for the oceanic case (right panel) corresponds to conductively cooling lithosphere with an age of 50 Myr joined by an adiabat with potential temperature of 1350°C. For cratons (Yilgarn and Northern Australia) the temperature profiles were constructed by forward modeling observed seismic velocities (Faul and Jackson, 2005; Jackson and Faul, 2010). The numbers show water content (in ppm H/Si). For cratonic temperatures diffusion creep and dislocation creep give very similar strain rates.

531 7. Conclusions

532 Experiments with synthetic, Ti-doped and silica-buffered olivine repro-
533 duce published parameters for the effect of water on the rheology of olivine.
534 Infrared spectra of the experimental samples show only two absorption bands,
535 at 3572 and 3525 cm^{-1} . These bands appear only in olivine that contains
536 Ti, independent of Si buffering. San Carlos olivine contains Ti, and cor-
537 respondingly the spectra of untreated samples, and those produced in low

538 water fugacity experiments exhibit these bands. The absence of IR bands
539 related to hydrated M-site vacancies in the products of the present exper-
540 iments indicates that the Ti-related defects are the cause for the observed
541 dependence of the rheology on water concentration. Hydration of Ti increases
542 the concentration of Si vacancies and therefore the Si diffusivity, consistent
543 with the view that Si diffusion is the rate limiting species for deformation of
544 olivine. Accounting for partitioning between solid phases, undepleted olivine
545 in the upper mantle contains enough Ti to accommodate the expected water
546 content of olivine in the asthenosphere (MORB-source mantle). Viscosities
547 calculated for the upper mantle based on published water contents are con-
548 sistent with viscosity estimates from the literature, indicating that Ti-related
549 hydrous defects can control the rheology of the upper mantle.

550 **Appendix A. Infrared Spectroscopy**

551 Room-temperature transmission FTIR spectra were recorded both after
552 hotpressing and after deformation for each sample at RSES, ANU using a
553 Bruker Tensor 27 spectrometer fitted with a Bruker Hyperion 2000 micro-
554 scope, a KBr beam splitter, a Globar light source and a MCT-A detector.
555 The microscope stage and spectrometer were continuously purged by nomi-
556 nally dry air. Spectra were recorded from 600 to 5000 cm^{-1} with a spectral
557 resolution of 4 cm^{-1} . The spectra in this study consist of the average of
558 128 scans. A 15x objective and a square aperture with a side length of 200
559 μm were used for all spectra. Spectra were recorded using unpolarised light
560 with approximately 400 μm thick sections that were polished on both sides.
561 The use of thick sections allows averaging of the absorbance over hundreds of

562 crystals (200 μm aperture, mean crystal size $\sim 25 \mu\text{m}$) with an appropriate
 563 correction for conversion to water content (Kovacs et al. (2008), see below
 564 Equation A.2).

565 Spectra were recorded from the center of the sample radially outwards
 566 to the rim with a spacing of $\sim 200 \mu\text{m}$ for a total of 25 to 30 spectra per
 567 sample. After the acquisition of each spectrum, an atmospheric compen-
 568 sation correction was applied to remove contributions from traces of water
 569 vapour, which improved the signal to noise ratio. Next, the background was
 570 fit using a concave rubber band baseline algorithm provided by the software,
 571 using three iterations, and subtracted. Alternative methods of background
 572 subtraction resulted in water contents that differed only by a few percent
 573 (Zhao et al., 2004; Bell et al., 2003). The concave rubber band method is
 574 reproducible and has little impact on the absorption bands (Kovacs et al.,
 575 2010; Padrón-Navarta et al., 2014).

576 Concentrations of molecular water and hydroxyl were separately calcu-
 577 lated by a Beer-Lambert law. Molecular water was calculated with:

$$C_{H_2O} = \frac{A(\nu = 3450\text{cm}^{-1})}{l \epsilon} \frac{M_{H_2O} \times 10^6}{\rho_{ol}}, \quad (\text{A.1})$$

578 where C is the concentration in wt. ppm, A is the measured absorbance
 579 at 3450 cm^{-1} , l is the sample thickness in cm and ϵ the molar absorption
 580 coefficient ($115 \text{ L mol}^{-1}\text{cm}^{-1}$, Clunie et al. (1966)). M_{H_2O} is the molar mass
 581 of water (18.02 g mol^{-1}) and ρ_{ol} is the density of olivine (3288 g l^{-1}).

582 The concentration of bound hydroxyl (in wt. ppm) was calculated from
 583 the integrated area under the absorption bands (A_{int}) as:

$$C_{OH} = \frac{A_{\text{int}} \times 3k}{l}. \quad (\text{A.2})$$

584 where k is the site-specific integral molar absorption coefficient, with a value
 585 of $k = 0.18 \text{ cm}^2$ for the Ti-defect site (Kovacs et al. (2010); see also Matveev
 586 and Stachel (2007) and discussion of hydrated defects in Section 5.2). The
 587 absence of an absorption band at 3612 cm^{-1} indicates that Si vacancies un-
 588 related to Ti were not protonated (Padrón-Navarta et al., 2014). The ori-
 589 entation factor of 3 relates the total water content to the absorbance from
 590 unpolarised spectra of randomly oriented crystals (Kovacs et al., 2008). A_{int}
 591 was determined between 3600 and 3450 cm^{-1} :

$$A_{\text{int}} = \int_{\nu=3450\text{cm}^{-1}}^{\nu=3600\text{cm}^{-1}} A(\nu) d\nu - \left\{ \frac{[A(\nu = 3600\text{cm}^{-1}) + A(\nu = 3450\text{cm}^{-1})](3600 - 3450)}{2} \right\}. \quad (\text{A.3})$$

592 The second term of equation A.3 subtracts the broad absorption region
 593 due to molecular water as indicated in Figure 4. A_{int} was calculated using
 594 the integration tool of the OPUS FTIR control software. As noted by Bell
 595 et al. (2003), the integration limits and subtraction of the molecular water are
 596 somewhat subjective, but results obtained from different treatments of the
 597 spectra typically agree within 5%. The absolute error involving integration
 598 limits and background correction is likely larger, with a conservative range
 599 from 10 - 30%.

600 Volumetric average hydroxyl and molecular water contents ($\overline{C}_i$, where i
 601 stands for either molecular or hydroxyl) for each sample were calculated from
 602 the respective radial variations after regularising the discrete measurements:

$$\overline{C}_i = \frac{1}{\pi R^2} \int_0^R 2\pi r [\text{H}_2\text{O}](r) dr, \quad (\text{A.4})$$

603 where R is the sample radius. The sample averaged molecular water content

604 thus obtained is with one exception significantly smaller than the averaged
605 hydroxyl content. The experiments are water-undersaturated since fH_2O is
606 not buffered. Accordingly we only observe one type of hydrated defect; at
607 saturated conditions and in equilibrium with orthopyroxene, hydrated metal
608 vacancies would also be expected (Berry et al., 2005; Kovacs et al., 2010).

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