



HAL
open science

Electrical conductivity anisotropy of dry and hydrous olivine at 8GPa

Brent T. Poe, Claudia Romano, Fabrizio Nestola, Joseph R. Smyth

► **To cite this version:**

Brent T. Poe, Claudia Romano, Fabrizio Nestola, Joseph R. Smyth. Electrical conductivity anisotropy of dry and hydrous olivine at 8GPa. *Physics of the Earth and Planetary Interiors*, 2010, 181 (3-4), pp.103. 10.1016/j.pepi.2010.05.003 . hal-00660106

HAL Id: hal-00660106

<https://hal.science/hal-00660106>

Submitted on 16 Jan 2012

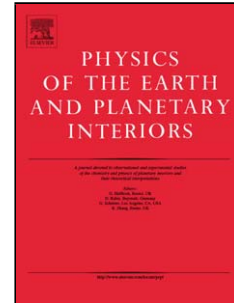
HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Accepted Manuscript

Title: Electrical conductivity anisotropy of dry and hydrous olivine at 8 GPa

Authors: Brent T. Poe, Claudia Romano, Fabrizio Nestola, Joseph R. Smyth



PII: S0031-9201(10)00102-0
DOI: doi:10.1016/j.pepi.2010.05.003
Reference: PEPI 5286

To appear in: *Physics of the Earth and Planetary Interiors*

Received date: 10-12-2009
Revised date: 3-5-2010
Accepted date: 18-5-2010

Please cite this article as: Poe, B.T., Romano, C., Nestola, F., Smyth, J.R., Electrical conductivity anisotropy of dry and hydrous olivine at 8 GPa, *Physics of the Earth and Planetary Interiors* (2008), doi:10.1016/j.pepi.2010.05.003

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

1 **Electrical conductivity anisotropy of dry and hydrous olivine**
2 **at 8 GPa**

3 Brent T. Poe^{a,b,*}, Claudia Romano^c, Fabrizio Nestola^d, Joseph R. Smyth^e

4 a. Dipartimento di Geotecnologie per l'Ambiente ed il Territorio, Università degli Studi
5 "G. d'Annunzio" – Chieti, Via dei Vestini 30, 66013 Chieti Scalo, Italy (Tel. +39-
6 0871-3556150, Fax +39-0871-3556047, email: poe@ingv.it)

7 b. Istituto Nazionale di Geofisica e Vulcanologia, Rome, Italy

8 c. Dipartimento di Scienze Geologiche, Università degli Studi di Roma Tre, Largo San
9 Leonardo Murialdo, 1, 00146 Rome, Italy (Tel. +39-06-53778018, email:
10 romano@uniroma3.it)

11 d. Dipartimento di Geoscienze, Università degli Studi di Padova, Via Giotto 1, 35137
12 Padova, Italy (Tel. +39-049-827-2009, email: Fabrizio.Nestola@unipd.it)

13 e. Department of Geological Sciences, University of Colorado, Boulder, CO 80309,
14 USA (Tel. +001-303 492 5521, email: smyth@colorado.edu)

15 *Corresponding author

16

17 ABSTRACT

18 The effects of dissolved H₂O on the electrical conductivity and its anisotropy in olivine
19 (Fo₉₀) at 8 GPa were investigated by complex impedance spectroscopy. At nominally
20 anhydrous conditions, conduction along [100] and [001] is slightly higher than along
21 [010] in contrast to observations made at lower pressures in earlier studies. Increasing
22 H₂O content increases conductivities but activation energies are lower and H₂O
23 concentration dependent. The use of polarized FTIR spectroscopy to determine H₂O
24 concentrations reveals a weaker than expected effect that water has on olivine
25 conductivity and distinguishes our results from earlier studies based on analyses using
26 non-polarized infrared spectroscopy. We show that at H₂O concentrations of a few
27 hundred wt ppm or less, that the dominant conduction mechanism at mantle
28 temperatures continues via small polarons, such as that observed for anhydrous olivine.
29 Our results also suggest that at depths greater than 200 km, the presence of H₂O may
30 not be necessary to explain regions in the upper mantle where both electrical and
31 seismic anisotropy are observed. This can be explained by differences in the pressure
32 dependence of the activation energy for conduction along each of the three
33 crystallographic axes. However, while electrical anisotropy of anhydrous olivine
34 remains weak at 8 GPa, it is nevertheless enhanced by elevated concentrations (>
35 several hundred wt ppm) of dissolved H₂O. At these conditions dominated by proton
36 hopping, conductivity along [010] is highest, approximately an order of magnitude
37 greater than along [100]. Additionally, at 1000 wt ppm and 1500°C, an isotropic
38 conductivity derived from the data is about 1 order of magnitude higher than that for
39 nominally anhydrous olivine. Thus, in regions of the mantle characterized by
40 anomalously high conductivities and both electrical and seismic anisotropy, significant
41 amounts of dissolved hydrogen can be expected.

42

43 Keywords: Electrical conductivity, high pressure, hydrous olivine, anisotropy

44

Accepted Manuscript

45 1. INTRODUCTION.

46 Recent studies have indicated that regions of electrical anisotropy in the mantle are
47 highly correlated to seismic anisotropy (Simpson, 2002; Eaton et al., 2004; Evans et al.,
48 2005) implying that knowledge of the electrical properties of olivine could provide
49 important insights regarding mantle flow. Lattice preferred orientation (LPO) of olivine
50 due to strain-induced deformation might account for observed electrical anisotropy at
51 depths beginning near 60 km depth in the oceanic mantle (Evans et al., 2005) and at
52 depths greater than 150 km below the North Central craton of Australia (Simpson,
53 2002). These observations lead to the suggestion that electrical conductivity in mantle
54 olivine must be highest parallel to the [100] direction. Schock et al. (1989) and Yoshino
55 et al. (2006) showed for single crystal olivine at 1 atm and 3 GPa, respectively, that at
56 upper mantle temperatures electrical conduction along the [100] direction is slower than
57 its other two principal crystallographic axes. However, in order to reconcile the
58 simultaneous presence of both electrical and seismic anisotropy, conduction along [100]
59 should be fast and parallel to the polarization direction of S-waves.

60 Laboratory data from Schock et al. (1989) and related models describing olivine
61 conductivity (Shankland and Duba, 1990; Constable et al., 1992) are also too resistive
62 to arrive at conductivities expected from models of magnetotelluric data corresponding
63 to the upper mantle (Gatzemeier and Moorkamp, 2005). Constable (2006) derived a
64 more recent model for dry olivine conduction which improves the agreement between
65 dry olivine conductivity and the upper mantle, particularly at temperatures above
66 1300°C. Nevertheless, the presence of H₂O in the mantle could possibly reconcile any
67 remaining differences between laboratory conductivity data of nominally anhydrous
68 minerals and EM profiles generated from magnetotelluric observations. Hydrogen
69 diffusion in olivine is faster than the mobility of intrinsic defects (Kohlstedt and

70 Mackwell, 1998), such that estimated conductivities of hydrous olivine through a proton
71 conduction mechanism are in better accord with upper mantle conductivity (Karato,
72 1990) and electrical anisotropy (Evans et al., 2005). Wang et al. (2006) measured
73 hydrous polycrystalline olivine conductivity at 4 GPa and concluded that 80 wt ppm
74 H₂O in olivine would increase its conductivity by more than a factor of ten at 1400°C
75 and account for the generally high conductivity of the oceanic asthenosphere. In
76 contrast, Yoshino et al. (2006) concluded that extrapolation of their data to higher
77 temperatures does not increase conductivity enough to explain the observed bulk
78 conductivity of the upper mantle. Yoshino et al. (2006), however, did not determine
79 how conductivity varies with varying water content along any of the three
80 crystallographic directions, but rather assumed that conductivity increased linearly with
81 H₂O concentration without change in activation energy. In a later study, Yoshino et al.
82 (2009) carried out additional experiments on hydrous polycrystalline aggregates of
83 olivine and determined the H₂O concentration dependence.

84 In this study, we investigate the electrical properties of single crystal San Carlos olivine
85 (Fo₉₀) as a function of dissolved H₂O content at 8 GPa using complex impedance
86 spectroscopy in a multianvil apparatus. We find that the higher pressure of this study
87 has a profound influence on electrical anisotropy compared to studies at lower pressure,
88 particularly for the case of hydrous olivine. We also find that significantly greater
89 concentrations of H₂O in olivine (ca. 1000 ppm) are required to increase olivine
90 conductivity by a factor of ten at upper mantle temperatures. In order to couple the
91 conductivity data with the elastic properties of olivine we have also investigated *in situ*
92 at high-pressure an anhydrous synthetic forsterite by single-crystal X-ray diffraction
93 using a diamond anvil cell.

94

95 2. EXPERIMENTAL METHODS

96 *2.1 Hydration of olivine single crystals.*

97 Oriented single crystals of San Carlos olivine (Fo₉₀) were machined into 1.8 mm dia. x
98 2 mm cylinders and placed in welded Pt capsules (2.0 mm o.d.) sandwiched between a
99 mixture of fine-grained synthetic talc (Mg₃Si₄O₁₀(OH)₂) and brucite (Mg₃(OH)₆)
100 (weight ratio 1.4:1). Hydration runs were carried out in a multianvil apparatus at
101 pressures ranging from 3 to 8 GPa and T=1100°C for up to 5 hours. Recovered single
102 crystals were then cut and polished into disc-shaped specimens (0.3 - 0.6 mm thick) for
103 complex impedance spectroscopy.

104 *2.2 Complex impedance spectroscopy.*

105 Complex impedances were measured at 8 GPa in either a 1000-tonne or 1200-tonne
106 Kawai-type multianvil apparatus using 11 mm truncation edge length tungsten carbide
107 anvils and 18 mm edge length MgO octahedra. The design of the conductivity cell is
108 described in detail by Poe and Xu (1999). The presence of a cylindrical Mo foil shield
109 lined with a small amount of MoO₂ powder is a key component of the cell. The shield is
110 placed between sample and furnace primarily to minimize interference between the
111 higher 50 Hz voltage applied to operate the furnace and the variable frequency signal
112 applied across the electrodes to measure complex impedance. Additionally, the shield is
113 grounded in common with the furnace to eliminate current leakage along the outer
114 surface of the sample and also serves as a fO₂ buffer according to the Mo + O₂ = MoO₂
115 equilibrium. Both Wang et al. (2006) and Yoshino et al. (2006) used Ni / NiO to buffer
116 their lower pressure experiments, whereas Yoshino et al. (2009) also used Mo /MoO₂ to
117 buffer their 10 GPa experiments. Measurements were made with a Solartron 1260
118 Impedance/Gainphase analyzer operating at 1.0 V amplitude and frequencies from 10⁵

119 to 10^{-1} Hz. A typical measurement consisted of heating to a maximum temperature,
120 depending on volatile content, and repeatedly acquiring the complex impedance
121 spectrum every 10 to 15 minutes until it remained unchanged (on the order of 1 hour).
122 Subsequent spectra were taken upon decreasing temperature only in order to maintain
123 the sample's H_2O concentration (measured post-run) in light of possible dehydration at
124 the maximum temperature of the measurement. It is quite likely that for the more H_2O -
125 rich samples, partial dehydration occurred at the maximum temperature (Yoshino et al.,
126 2006). However, afterwards, at lower temperatures, observed Arrhenian behavior would
127 suggest a negligible amount of additional dehydration. The complex impedance data
128 were fit to an expression for an RC parallel equivalent circuit, allowing for some
129 deviation ($< 10^\circ$) of the circle center from the real axis. From the determined resistance
130 and the sample and electrode dimensions, electrical conductivity was determined.
131 Experimental error, arising mainly from uncertainties in the sample dimensions and any
132 non-ideality of the form of the data with respect to the equivalent circuit, is estimated to
133 be about 5% relative.

134 *2.3 Polarized FTIR spectroscopy.*

135 Samples recovered after complex impedance spectroscopy were analyzed by polarized
136 infrared spectroscopy using a Bruker IFS 120 HR high resolution Fourier-transform
137 spectrometer and IR microscope with Cassegranian optics. The concentration of
138 dissolved H_2O in olivine was determined using the calibration of Bell et al., (2003) who
139 showed that the calibration of Paterson (1982) for unpolarized FTIR spectra may
140 underestimate water content in olivine by a factor of 2-4 owing to the extreme IR
141 pleochroism of olivine. Table 1 lists H_2O concentrations (in wt ppm) for samples after
142 complex impedance measurements. Similar to previous observations (Mosenfelder et
143 al., 2006; Smyth et al., 2006; Kohlstedt et al., 1996) for laboratory-synthesized H_2O -

144 rich samples, multiple absorption bands in the range 3300-3500 cm^{-1} are observed in
145 addition to the main peaks between 3500 and 3600 cm^{-1} .

146 *2.4 Single crystal XRD.*

147 In order to better understand how differences in electrical conductivity might be related
148 to structural changes to the crystal lattice at these conditions, we also performed a series
149 of single crystal X-ray diffraction measurements. A colorless single crystal of pure
150 forsterite, free of twins and inclusions, was synthesized at room pressure and 1600°C.
151 Although the chemical composition of the crystal was slightly different to those of the
152 electrical measurements, we assume that the general behavior observed can be useful to
153 our interpretation of the conductivity results. The crystal, with dimensions 80×60×50
154 μm^3 , was loaded in a BGI-type diamond-anvil cell (DAC) with T301 steel foil gasket. A
155 mixture of methanol:ethanol (4:1) served as pressure-transmitting medium. A quartz
156 crystal was added as an internal pressure standard (Angel et al. 1997). Unit-cell
157 parameters (Table 1) were determined at 19 different pressures up to about 6.8 GPa and
158 room temperature on a Huber four-circle diffractometer (non-monochromatized $\text{Mo}_{\text{K}\alpha}$
159 radiation) using eight-position centering of not less than 20-22 Bragg reflections
160 according to the procedure of King and Finger (1979). Centering procedures and vector-
161 least-square refinement of the unit-cell constants were performed using the SINGLE04
162 software (Angel et al. 2001) according to the protocols of Ralph and Finger (1982)
163 without any symmetry constraints in order to monitor possible high-pressure phase
164 transformations. The unit-cell parameters data at each pressure are reported in Table 1.

165 3. RESULTS AND DISCUSSION

166 *3.1 Hydrogen incorporation in olivine.*

167 The solubility of hydrogen in olivine is low compared to its higher pressure polymorphs
168 wadsleyite and ringwoodite (Kohlstedt et al., 1998). However, recent studies that
169 utilized polarized FTIR spectroscopy have shown that H₂O solubility in olivine is
170 higher by as much or more than a factor of two compared to previous studies that used
171 non-polarized FTIR spectroscopy (Bell et al., 2003; Mosenfelder et al., 2006). An
172 example of our polarized FTIR spectra is shown in Fig. 1 for the H₂O-rich sample
173 S3740. Absorption is strongest with the electric field gradient, E, oriented parallel to the
174 *a*-axis, consistent with the observations of previous studies (Kohlstedt et al., 1998; Bell
175 et al., 2003; Mosenfelder et al., 2006). Also, similar to Kohlstedt et al. (1998) we
176 observe several strong absorption bands at lower OH stretching frequencies (3300-3500
177 cm⁻¹) in our synthetically hydrated samples which do not appear in the spectra of natural
178 olivine samples having much lower H₂O concentrations (Mosenfelder et al., 2006).
179 Differences between the spectra of synthetically hydrated and natural olivine specimens
180 illustrate that hydrogen incorporation in olivine is a complex function of oxygen
181 fugacity and silica activity in addition to water fugacity (Mosenfelder et al., 2006). The
182 pressure of the hydration experiments varied from 3 to 8 GPa in order to vary water
183 fugacity and resulted in a range of H₂O concentrations from 363 to 2215 wt ppm (see
184 Table 1), based on the calibration of Bell et al. (2003) for polarized FTIR spectra.
185 Interestingly, in earlier attempts to hydrate single crystals of olivine using a piston
186 cylinder apparatus (up to 3 GPa) the recovered run products were often opaque and/or
187 fractured such they could not be used for conductivity measurements. Uncertainties in
188 the effect of H₂O on conductivity are primarily related to these analyses, however, as
189 spectra could be obtained only post electrical measurement in order to preserve sample
190 geometry and orientation for determination of its conductivity. Additional sources of
191 error in the H₂O concentrations stem from inhomogeneities revealed upon reducing the

192 size of the aperture (< ca. 600 μm^2) and uncertainties in baseline subtraction owing to
193 spectra composed of very broad and overlapping absorption bands.

194 3.2 Complex impedance spectra.

195 A representative suite of complex impedance spectra for a hydrated single crystal of
196 olivine oriented along its (100) axis (H2474) is shown in Fig. 2. Each spectrum is
197 characterized by a semi-circular pattern of data spanning from the axes origin at the
198 highest frequencies, reaching a minimum imaginary component (Z'') and returning
199 toward the abscissa with increasing real impedance (Z') at very low frequencies. With
200 increasing temperature, the shape of the spectrum remains semi-circular and its
201 diameter, which is proportional to the sample's electrical resistance, decreases. We note
202 that with decreasing frequency, particularly at lower temperatures (see Fig. 2), the
203 scatter in the data markedly increases, most likely due to increasingly higher
204 impedances. While it has been assumed in several previously published studies that the
205 measured impedance at a single frequency, provided that the frequency is sufficiently
206 low, may be equal to the sample resistance (Schock et al., 1989; Fu-jita et al., 2004,
207 Yoshino et al., 2008), such an assumption in our case would lead to large uncertainties.
208 Over the experimental spectral range, spanning 6 decades in frequency, a majority of
209 the semicircular arc is observed, providing a lower uncertainty of the sample resistance
210 compared to any single low frequency measurement.

211 Conductivities are shown for each crystallographic direction at anhydrous and various
212 concentrations of dissolved H_2O in Fig. 3. For each individual sample log conductivity
213 decreases linearly with reciprocal temperature according to the Arrhenius expression

$$214 \quad \sigma = \sigma_0 \exp(-H/kT) \quad \text{Eq. 1}$$

215 where k is the Boltzmann constant, T the absolute temperature and $\log \sigma_0$ and H the
216 intercept and slope, respectively, of the linear regressions. Best fit values of the pre-
217 exponential term σ_0 and the activation enthalpy H for each experiment are listed in
218 Table 2 along with crystallographic orientation and measured H_2O concentration.
219 Because the correlation of the data to Eq. 1 is very high in all cases, we have assumed
220 that H_2O concentration during the electrical measurement remained constant and equal
221 to that of the post-measurement FTIR analysis of the sample. Although it is not
222 observed here, non-Arrhenian behavior would likely be the result of either a change in
223 chemical composition during the measurement, such as loss of dissolved H_2O , or from a
224 temperature dependent change in the conductivity mechanism. In the former case, such
225 behavior would be irreversible with temperature, whereas in the latter case, we can
226 expect the behavior to be reversible and characterized by a stronger temperature
227 dependence (higher H) at lower $1/T$.

228 *3.3 Electrical conductivity of dry olivine.*

229 For the anhydrous samples, conductivities were determined at temperatures ranging
230 from 850 to 1436°C, overlapping both the small polaron and Mg vacancy conduction
231 regimes expected as the dominant charge transport mechanisms at low and high
232 temperatures, respectively at 1 atm (Schock et al., 1989; Hirsch et al., 1993; Constable
233 and Roberts, 1997; Dufrane et al., 2005). Also shown in Fig. 3 are the results of
234 Yoshino et al. (2006) obtained at 3 GPa, in very good agreement with our data for
235 anhydrous olivine. Given that our measurements were carried out at 8 GPa, the
236 agreement among our data and those of Yoshino et al. (2006) strongly reflects the low
237 activation volume ($< 1 \text{ cm}^3/\text{mol}$) for electrical conduction of olivine determined by Xu
238 et al. (2000). A low activation volume also supports the notion that the conduction
239 mechanism is electronic, such as via small polarons which involves the hopping of

240 electron holes. In contrast, an ionic conduction mechanism involving the hopping of
241 ionic species and vacancies, would require lattice distortions resulting in highly positive
242 activation volumes on the order of several cm^3/mol (Keyes, 1963; Samara, 1984). The
243 absence of a second conduction mechanism which would otherwise be indicated by a
244 break in slope in the data shown in Fig. 3 (open red triangles) suggests that the
245 conductivity is governed predominantly through small polarons, even at temperatures as
246 high as 1436°C . We note that Yoshino et al. (2009) did observe ionic conduction in
247 their dry polycrystalline olivine at 10 GPa. However, they report that small polaron
248 conduction continues up to 1477°C , with ionic conduction taking over at higher
249 temperatures up to their maximum $T=1727^\circ\text{C}$.

250 The lower pressure studies of both Shock et al. (1989) and Yoshino et al. (2006)
251 indicate that conduction along [100] is lower compared to one or both of the other
252 crystallographic directions. Despite the seemingly good agreement illustrated in Fig. 3
253 between our data and those of Yoshino et al. (2006) at anhydrous conditions, at 8 GPa
254 and 1200°C we find that conduction along [100] and [001] are about equal and
255 approximately 0.2 log units higher compared to [010]. This difference can be attributed
256 to the small, but distinct changes in activation enthalpy from 3 to 8 GPa along each
257 crystallographic axis. While the activation enthalpy for conduction along [100] remains
258 high, it is reduced along both [010] and [001] in comparison to those at 3 GPa reported
259 by Yoshino et al. (2006). A reduction in activation enthalpy with increasing pressure,
260 here for the case of small polaron conduction, can be explained by decreasing
261 interatomic distances between Fe^{2+} and Fe^{3+} , which facilitate the electron hole hopping
262 mechanism.

263 Results from our single crystal diffraction measurements of forsterite up to 6.7 GPa
264 indicate that the [100] direction is the least compressible of the three axes, in good

265 agreement with other recent in-situ single crystal x-ray diffraction studies (Liu and Lee,
266 2006; Katsura et al., 2009) and with resonant ultrasonic spectroscopy (Isaak et al.,
267 1989). At high pressure, interatomic distances would thus be shortened more along both
268 the *b* and *c* directions compared to the *a* direction (Fig. 4). A more rapidly changing cell
269 parameter is likely to be accompanied by a greater change in activation energy for
270 conduction in that direction. Thus, at 8 GPa and the higher temperatures associated with
271 the deeper upper mantle, conductivity along [100] becomes higher than [010], opposite
272 to that which is observed at ambient pressure (Schock et al., 1989) and at 3 GPa
273 (Yoshino et al., 2006).

274 For dry olivine conductivity anisotropy remains relatively weak because of the minor
275 changes in temperature dependence from 3 to 8 GPa. However, the higher conductivity
276 along [100] presents important implications where both electrical and seismic
277 anisotropy are observed in the upper mantle. Because both high conductivities and fast
278 shear wave velocities cannot be rationalized by LPO in dry olivine at shallow depths (\leq
279 3 GPa), the presence of dissolved H₂O in olivine has been suggested as responsible for
280 favoring conduction along [100] via a fast proton conduction mechanism (Evans et al.,
281 2005). Based on our data at 8 GPa corresponding to greater depths (> 200 km), proton
282 diffusion is not required to justify a higher conductivity along [100] and the observed
283 electrical anisotropy at these depths, such as below the North Central craton of Australia
284 (Simpson, 2002). Because the effects of pressure and temperature on the electrical
285 conductivity of dry olivine are different along each crystallographic direction, electrical
286 anisotropy changes with depth in the mantle without requiring the presence of dissolved
287 hydrogen to invoke a different conduction mechanism. The absence of an ionic
288 conduction pathway at 8 GPa may also contribute to the difference in anisotropy that is
289 observed at 3 GPa (Yoshino et al., 2006). We also stress that this conclusion can be

290 drawn independently of our conductivity results for hydrous olivine which are discussed
291 below (Section 3.4), and therefore is not compromised by the additional experimental
292 uncertainties due to analyses of H₂O content nor by long extrapolations of those data to
293 the higher temperatures associated with the mantle.

294 If we apply the geometric mean of the three data sets to generate an isotropic model for
295 dry olivine conductivity, we find that at 8 GPa and 1200°C conductivity is 2.97×10^{-3}
296 S/m, in very close agreement with the geometric mean of 2.14×10^{-3} S/m at the same
297 temperature calculated using the results of Yoshino et al. (2006) at 3 GPa and a value of
298 2.02×10^{-3} S/m at 10 GPa using the results of Yoshino et al. (2009). Both of these
299 values compare well to mantle conductivity values below the Canadian shield (Neal et
300 al., 2000) and below the French Alps (Tarits et al., 2004) using a standard geotherm to
301 extract a comparative temperature from the MT profiles. These values, however, are
302 low in comparison to the oceanic mantle at the same temperature (Evans et al., 2005).
303 Thus, while our data for dry olivine at 8 GPa may reconcile both electrical and seismic
304 anisotropy at deep continental mantle depths, we must still explore the effect of water
305 on electrical anisotropy where there may be poor agreement in the absolute electrical
306 conductivity.

307 *3.4 Hydrous olivine conductivity.*

308 For the hydrous olivine samples, temperatures did not exceed 700°C during the
309 measurement in order to minimize possible dehydration of the sample. We can not
310 exclude the possibility that the dominant conduction mechanism in hydrous olivine
311 changes at temperatures above 700°C. However, Wang et al (2006) measured the
312 conductivity of polycrystalline hydrous olivine at temperatures as high as 1000°C and
313 determined an activation enthalpy of 87 kJ/mol (ca. 0.9 eV), significantly lower than

314 that for dry olivine conduction and similar to the activation enthalpies observed in this
 315 study at lower H₂O concentrations (see Table 2).

316 In Fig. 3 we see that the effect of dissolved H₂O in olivine is to increase its conductivity
 317 while decreasing its activation energy. Thus, the effect of H₂O on conductivity
 318 diminishes with increasing temperature. Yoshino et al. (2006) measured only one
 319 hydrous olivine sample for each crystallographic direction, and thus would not have
 320 been able to recognize this trend if it were present at 3 GPa. Yoshino et al. (2009),
 321 however, did observe this behavior in their later study of polycrystalline olivine at 10
 322 GPa and also for conductivities of hydrous wadsleyite and hydrous ringwoodite
 323 (Yoshino et al., 2008), which are high pressure polymorphs of olivine. They suggested
 324 that increasing H₂O content in these phases resulted in behavior similar to that of N-
 325 type semiconductors, according to the equation

$$326 \quad \sigma = \sigma_0 C_w \exp\left(-\frac{H - \alpha C_w^{1/3}}{kT}\right) \quad (\text{Eq. 2})$$

327 In the case of hydrous olivine, Yoshino et al. (2006), Wang et al (2006) and Yoshino et
 328 al. (2009) also determined their H₂O concentrations using FTIR spectroscopy, but all
 329 according to the calibration of Paterson (1982) for non-polarized spectra. Our H₂O
 330 determinations are based on the calibration of polarized FTIR spectra by Bell et al.
 331 (2003), who demonstrated its importance for pleochroic minerals. Mosenfelder et al.
 332 (2006) recently pointed out that use of the Paterson calibration for determining
 333 dissolved H₂O concentrations in Fe-bearing olivine can underestimate concentrations by
 334 as much as a factor of 4 compared to its determination by the calibration of Bell et al.
 335 (2003). The use of a different FTIR calibration may contribute to the differences in the
 336 effect of dissolved H₂O on the conductivity of olivine in our study compared to the
 337 study of Yoshino et al. (2006). If the H₂O concentrations from Yoshino et al. (2006)

338 were underestimated due to their use of the Paterson calibration, then the effect of
339 dissolved H₂O on olivine conductivity that they report would be overestimated by a
340 similar factor.

341 We have chosen to fit the hydrous olivine data separately from the anhydrous data based
342 on two observations upon examination of Fig. 3 and Table 2. Most importantly,
343 individual datasets show strongly Arrhenian behavior, which allows us to assume that a
344 single charge transport process dominates each sample's electrical conductivity. Slight
345 changes in slope are detectable only in the case of conduction along [100] at the lowest
346 H₂O concentration and along [001] at the highest H₂O concentration (Fig. 3). Because
347 we do not observe any systematic occurrence, rather than indicating a change in
348 conduction mechanism, this behavior may be related to some form of experimental
349 factor, such as insufficient time allowed for sample re-equilibration at lower
350 temperatures. Secondly, activation enthalpies are clearly lower and most likely H₂O
351 concentration dependent for the hydrous olivine data. This latter observation suggests
352 that the dominant mechanism in hydrous olivine can not be the same as that for
353 anhydrous olivine.

354 Our fits of Eq. 2 to the hydrous olivine conductivity data for each of the three
355 crystallographic orientations are also illustrated in Fig. 3. We note that within
356 experimental error, these H₂O concentration dependent approximations are in excellent
357 agreement with the simple Arrhenian fits to each individual dataset. Best fit parameters
358 are listed in Table 3. Also shown in Fig. 3 are the approximations reported by Yoshino
359 et al. (2006) for dry and [H₂O]-independent hydrous olivine conductivity. We can
360 compare our results to those for hydrous, polycrystalline olivine (Yoshino et al., 2009)
361 and its higher pressure polymorphs wadsleyite and ringwoodite (Yoshino et al., 2008) in
362 which the same form of Eq. 2 was used (note that both Yoshino et al. 2008 and 2009

363 use concentration units of wt% rather than wt ppm and we convert their values of σ_0 and
364 α accordingly for comparison below). Our best fit values for σ_0 range from ca. 0.001
365 S/m along [100] to 0.3 S/m along [010]. These values are in excellent agreement with
366 that for the proton conduction term from Yoshino et al. (2009), $\sigma_0 = 0.0079$, as well as
367 their study of hydrous wadsleyite and ringwoodite, with $\sigma_0 = 0.008$ and 0.0028 S/m,
368 respectively (Yoshino et al., 2008). The best fit values of H from Eq. 2 range from 0.8
369 eV along [001] to 1.5 eV along [010], in good agreement with 0.92 eV for
370 polycrystalline olivine from Yoshino et al. (2009) and the values of 0.7 and 1.1 eV for
371 wadsleyite and ringwoodite, respectively (Yoshino et al., 2008). Finally, the H₂O-
372 concentration dependence parameter, α , ranges from 0.03 to ca. 0.07, which, according
373 to Eq. 2 results in a progressively shallower slope of $\log \sigma$ vs. $1/T$ with increasing H₂O
374 content. The values of α from Yoshino et al. (2009) for olivine and from Yoshino et al.
375 (2008) for wadsleyite and ringwoodite range between 9×10^{-4} to 0.03.

376 We also fit the equation used by Wang et al (2006) to our data for hydrous olivine. The
377 form of the equation and results from those fits are also given in Table 3. Similar to Eq.
378 2, the pre-exponential term is concentration dependent, but includes two adjustable
379 parameters, σ_0 and r . Here we find that the σ_0 term returns a very large relative error.
380 Additionally, the higher χ^2 values from this fit compared to the fit using Eq. 2 are the
381 result of a fixed rather than H₂O concentration dependent activation enthalpy, even
382 though the total number of adjustable parameters is the same for both fits. Interestingly,
383 the best fit values for the exponent r (from about 2.5 along [100] to 3.5 along [010] and
384 [001]) are much higher than that determined by Wang et al (2006) for hydrous
385 polycrystalline olivine (ca. 0.6). As Wang et al. (2006) discussed, the value of r is
386 indicative of the type of defect mechanism that controls proton hopping. Romano et al
387 (2009) measured the electrical conductivity of hydrous wadsleyite and determined a

388 best-fit value of $r = 1.44$ using the same equation. As stated previously, the higher
389 temperature measurements of Wang et al (2006) may explain some of the differences
390 from our study as the mechanism for conduction may change with increasing
391 temperature. Indeed, Wang et al. (2006) assumed that both small polaron and proton
392 hopping conduction mechanisms contributed to the bulk conductivity at high
393 temperature, such that the fits to their data included both a dry (small polaron)
394 component and a wet (proton hopping) component. However, it is clear that at lower
395 temperatures, the temperature dependence for conductivity is strongly coupled to
396 dissolved water content in olivine such that Eq. 2 provides a much more robust
397 approximation of the experimental data.

398 *3.5 Important differences from previous studies.* A comparison of our results to those
399 from Wang et al. (2006) and Yoshino et al. (2006) is made difficult because of the
400 pressure effects that are likely to play a role between 3 or 4 GPa and 8 GPa. Regardless
401 of such effects, however, neither Wang et al. (2006) nor Yoshino et al. (2006)
402 demonstrate any link between temperature dependence of conductivity and H₂O
403 concentration. Our results show that activation enthalpy decreases with increasing water
404 concentration. This observation not only indicates that the proton hopping mechanism
405 becomes less important at higher temperatures as small polaron conduction begins to
406 dominate, but also that the effect of dissolved water diminishes with increasing
407 temperature. Yoshino et al. (2009) later investigated the effect of water concentration at
408 10 GPa, but on polycrystalline olivine aggregates. Their study, like ours, observes small
409 polaron conduction to temperatures above 1700 K in nominally anhydrous samples.
410 Similar to our results, Yoshino et al. (2009) show that activation enthalpy decreases
411 with increasing H₂O content, but their dependence (α term, Table 3) is less than what is
412 observed here. The reason for this difference is still unclear as the pressures and

413 temperatures of both studies are quite similar. The major differences in the experimental
414 approach are that Yoshino et al. (2009) used polycrystalline samples, non-polarized
415 FTIR spectroscopy and a corresponding FTIR calibration by Paterson (1982) whereas
416 our study examined single crystal samples, and determined H₂O contents using
417 polarized FTIR and calibration by Bell et al. (2003).

418 The fit to Eq. 2 allows us to determine electrical anisotropy, given simply by the
419 difference between $\log \sigma_{\max}$ and $\log \sigma_{\min}$ among the three different crystallographic
420 directions as a function of temperature, shown for nominally anhydrous olivine and at
421 H₂O concentrations of 100 and 1000 wt ppm in Fig. 5. We can justify extrapolation of
422 the hydrous data to higher temperatures as the conductivities remain higher than those
423 for dry olivine, except in the case of [001] above 1350°C at the lowest H₂O
424 concentration (see Fig. 3). No extrapolations are made for dry olivine for which
425 electrical anisotropy is determined using the fit parameters to the Arrhenius expression
426 (Table 2). For both anhydrous olivine and at 100 ppm wt H₂O, conduction along [100]
427 remains highest. Interestingly, at 100 wt ppm H₂O, electrical conductivity is more
428 isotropic than that of dry olivine. However, at 1000 wt ppm H₂O, electrical anisotropy is
429 greater, by about a factor of ten along [010] compared to the [001] direction. At these
430 H₂O rich conditions, anisotropy is nearly independent of temperature. The complex
431 behavior we observe over this range of H₂O content could be related to the speciation of
432 H₂O in olivine as a function of its concentration, which is still poorly understood at
433 present. Hushur et al. (2009) report that the high pressure hydration mechanism in
434 forsterite is principally M1 site vacancy with the proton on the O1-O2 edge shared
435 between M1 octahedra. This mechanism would increase *c*-axis compressibility and
436 facilitate proton movement along the edge-sharing M1 octahedral chains parallel to *c*.
437 We would then expect a lower activation enthalpy along *c* compared to *b* for conduction

438 dominated by proton hopping (see Table 3) much like what we observe for the
 439 anhydrous case of small polaron hopping where *b*-axis compressibility is greatest (Fig.
 440 4) and its activation enthalpy lowest (Table 2). This would of course influence its
 441 anisotropy but in a different manner compared to anhydrous olivine or H₂O-poor olivine
 442 for which the dominant conduction mechanism may be unrelated to the presence of
 443 hydrogen (see below Section 3.6).

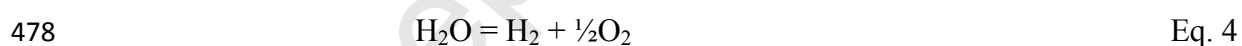
444 3.6 Competing charge transport mechanisms.

445 It is important to note that the anhydrous data are not included in the fit to Eq. 2 because
 446 the conduction process cannot involve a protonated charge carrier. Even at low H₂O
 447 concentrations, the activation enthalpy is lower than that for anhydrous olivine, such
 448 that at higher temperatures it would be expected to intersect the anhydrous data. This
 449 suggests that electrical conduction in hydrous olivine is dominated by a proton-bearing
 450 charge carrier at low temperatures but crosses over to the small polaron conduction
 451 mechanism at a temperature that depends on the H₂O concentration. By combining the
 452 results of the fits to Eq. 2 for hydrous olivine with the best fit parameters to the
 453 Arrhenius equation for the anhydrous data, we can determine the temperature of this
 454 crossover for the total geometric mean electrical conductivity, which is equal to the sum
 455 of the small polaron (σ_{Fe}) and proton (σ_{H}) geometric mean conductivities

$$456 \quad \sigma = \left(\sigma_{\text{Fe}100} \cdot \sigma_{\text{Fe}010} \cdot \sigma_{\text{Fe}001} \right)^{\frac{1}{3}} + \left(\sigma_{\text{H}100} \cdot \sigma_{\text{H}010} \cdot \sigma_{\text{H}001} \right)^{\frac{1}{3}} \quad \text{Eq. 3}$$

457 Figure 6a illustrates the variation of $\log \sigma$ with H₂O concentration and temperature and
 458 the boundary between the small polaron dominant and H-bearing dominant fields. The
 459 cross-over temperature indicated by the dashed black line increases smoothly with \log
 460 [H₂O]. We find that the slope of the boundary is quite steep due to the large change in
 461 activation energy with increasing H₂O content. At H₂O concentrations below a few

462 hundred wt ppm, the dominant charge transport mechanism is that of small polarons.
463 Fig. 6b shows similar behavior using the results of Yoshino et al. (2009). At the far left
464 of the plot beginning at 10 wt ppm H₂O, which corresponds to small polaron
465 conduction, the two models are in very good agreement. Only at the highest
466 temperatures, at which Yoshino et al. (2009) observe ionic conduction, do the nominally
467 anhydrous conductivities begin to diverge. For hydrous olivine, our results show that
468 the strong H₂O concentration dependence of the cross-over temperature implies that
469 significant concentrations of dissolved H₂O (several hundred wt ppm) could cause the
470 mantle to switch from small polaron to proton hopping conduction. The results from
471 Yoshino et al. (2009), however, would indicate this to be less likely due to a weaker
472 H₂O concentration dependence. We have assumed that the effect of H₂O on the small
473 polaron mechanism has a negligible effect on the anhydrous conductivity simply
474 because we have no conductivity data for hydrous olivine at sufficiently high
475 temperatures that might be suggestive of a different conduction mechanism. However, it
476 is likely that dissolved H₂O in olivine also influences the small polaron conductivity
477 indirectly through its effect on the fO₂ via autodissociation,



479 and how the change in oxidation state influences the ratio of ferric to ferrous iron. Thus,
480 the effect is likely to be slightly positive, and therefore the boundaries shown in Fig. 6
481 would represent the minimum temperature of the crossover.

482 *3.6 Conclusions.*

483 As mentioned above, with increasing temperature the effect of H₂O concentration
484 diminishes. However at 1500°C, the calculated isotropic conductivity (geometric mean)
485 at 1000 ppm H₂O remains a factor of ten higher than that for nominally anhydrous

486 olivine. We conclude that in the deeper half of the upper mantle, both the absolute
487 conductivity and electrical anisotropy of H₂O-bearing olivine can indeed account for
488 observed magnetotelluric signatures which result in either anomalously high
489 conductivities or strong anisotropy associated with similar anomalously high shear
490 velocities. In other words, in the deeper regions of the upper mantle where both the
491 absolute conductivity and electrical anisotropy are anomalously high, we cannot rule
492 out the possibility that high concentrations of dissolved H₂O (several hundred wt ppm
493 or more) in olivine may be present.

494 We must also note that variations in both silica and oxygen activities play important
495 roles on the electrical properties of olivine (Wanamaker and Duba, 1993; Du Frane et
496 al., 2005). Although we have not addressed these chemical parameters in our study, it is
497 clear that small changes in H₂O concentration still result in measureable changes in
498 electrical conductivity. Within the dry olivine stability field, Du Frane et al. (2005)
499 demonstrated that a difference of more than five orders of magnitude in fO₂ is required
500 to change its conductivity by a factor of ten. Within the chemical environment defined
501 by our experiments, conceivable lateral variations in H₂O concentration from nominally
502 anhydrous to 0.1 wt% can achieve the same relative change.

503 Lastly, we emphasize that the effect of H₂O on the electrical conductivity of olivine is
504 pressure, temperature and H₂O concentration dependent. Our results show that these
505 effects are not as large as previously suggested, possibly due to differences in both
506 experimental and analytical approaches. Most importantly, because the activation
507 energy for H-bearing conduction mechanisms are significantly lower than those for
508 electronic conduction, these effects become less important with increasing depth (i.e.
509 increasing temperature) in the mantle. Unfortunately, this also implies that experimental
510 studies to determine the electrical conductivity of hydrous phases stable at lower mantle

511 conditions may not necessarily be useful in constraining the water content at very deep
512 mantle depths.

513 ACKNOWLEDGEMENTS

514 We are grateful to H. Fisher and H. Schulze of the Bayerisches Geoinstitut (University
515 of Bayreuth) for technical assistance. High-pressure experiments were performed at the
516 Bayerisches Geoinstitut under the EU "Research Infrastructures: Transnational Access"
517 Programme (Contract No. 505320 (RITA) - High Pressure). We also thank two
518 anonymous reviewers for their helpful comments.

519 REFERENCES

520 Angel, R.J., D.R. Allan, R. Miletich, L.W. Finger (1997) The use of quartz as an
521 internal pressure standard in high-pressure crystallography. *Journal of Applied*
522 *Crystallography*, 30, 461-466.

523 Angel, R.J., R.T. Downs, L.W. Finger (2001) High-Temperature-High-Pressure
524 Diffraction. In Hazen, R.M., Downs, R.T. (Eds.), *High-pressure, high-temperature*
525 *crystal chemistry. Reviews in Mineralogy and Geochemistry*, 41, 559-596.

526 Bell, D. R., G. R. Rossman, J. Maldener, D. Endisch, F. Rauch, (2003), Hydroxide in
527 olivine: a quantitative determination of the absolute amount and calibration of the IR
528 spectrum, *J. Geophys. Res.*, 108(2105), 10.1029/2001JB000679.

529 Constable, S. (2006) SEO3: a new model of olivine electrical conductivity. *Geophys. J.*
530 *Int.* 166, 435-437.

531 Constable, S. and J. J. Roberts (1997) Simultaneous modelling of thermopower and
532 electrical conduction in olivine, *Phys. Chem. Min.*, 24, 319-325.

533 Constable, S. C., T. J. Shankland, and A. G. Duba (1992) The electrical conductivity of
534 an isotropic olivine mantle, *J. Geophys. Res.*, 97, 3397-3404.

535 Du Frane, W. L., J. J. Roberts, D. A. Toffelmier, and J. A. Tyburczy (2005), Anisotropy
536 of electrical conductivity in dry olivine, *Geophys. Res. Lett.*, 32, 24315, doi:
537 10.1029/2005GL023879.

538 Eaton, D. W., A. G. Jones, and I. J. Ferguson (2004), Lithospheric anisotropy structure
539 inferred from collocated teleseismic and magnetotelluric observations: Great Slave Lake
540 shear zone, northern Canada, *Geophys. Res. Lett.*, 31, L19614, doi:
541 10.1029/2004GL020939.

- 542 Evans, R. L., G. Hirth, K. Baba, D. Forsyth, A. Chave, and R. Mackie (2005),
543 Geophysical evidence from the MELT area for compositional controls on oceanic
544 plates, *Nature*, 437, 249-252.
- 545 Fu-jita, K., T. Katsura and Y. Tainosho (2004), Electrical conductivity measurement of
546 granulite under mid- to lower crustal pressure-temperature conditions. *Geophys. J. Int.*
547 157, 79-86.
- 548 Gatzemeier, A. and M. Moorkamp (2005) 3D modelling of electrical anisotropy from
549 electromagnetic array data: hypothesis testing for different upper mantle conduction
550 mechanisms, *Phys. Earth Planet. Int.*, 149, 225-242.
- 551 Hirsch, L.M., Shankland, T.J., Duba, A.G., 1993. Electrical conductivity and polaron
552 mobility in Fe-bearing olivine. *Geophys. J. Int.* 114, 36–44.
553
- 554 Hushur, A., M.H. Manghnani, J. R. Smyth, F. Nestola, and D.J. Frost (2009) Crystal
555 chemistry of hydrous forsterite and its vibrational properties up to 41 GPa. *Am.*
556 *Mineral.* 94 (in press).
- 557 Isaak, D.G., Anderson, O.L., Goto, T. (1989). Elasticity of single crystal forsterite
558 measured to 1700 K. *J. Geophys. Res.* 94, 5895–5906.
559
- 560 Karato, S. (1990) The role of hydrogen in the electrical-conductivity of the upper
561 mantle, *Nature*, 347(6290), 272– 273.
- 562 Katsura, T., et al., (2009) Thermal expansion of forsterite at high pressures determined
563 by in situ x-ray diffraction: the adiabatic geotherm in the upper mantle. *Phys. Earth*
564 *Planet. Int.*, in press.

- 565 Keyes, R.W., 1963. Continuum models of the effect of pressure on activated process.
566 In: Paul, W., Warschauer, D.M._Eds., Solids Under Pressure. McGraw-Hill, New
567 York, pp. 71–99.
- 568 King, H.E. and L. Finger (1979) Diffracted beam crystal centering and its application to
569 high pressure crystallography. *Journal of Applied Crystallography*, 12, 374–378.
- 570 Kohlstedt, D. L. and S. J. Mackwell (1998) Diffusion of hydrogen and point defects in
571 olivine, *Z. Phys. Chem.*, 207, 147-162.
- 572 Liu, W. and Lee, B. (2006) Thermal equation of state of $(\text{Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4$ olivine.
573 *Phys. Earth Planet. Int.* 157, 188-195.
- 574 Mosenfelder, J. L., N.I. Deligne, P. D. Asimov, G. R. Rossman (2006) Hydrogen
575 incorporation in olivine from 2-12 GPa, *Amer. Mineral.*, 91, 285-294.
- 576 Neal, S. L., R. L. Mackie, J. C. Larsen, and A. Schultz (2000) Variations in the
577 electrical conductivity of the upper mantle beneath North America and the Pacific
578 Ocean. *J. Geophys. Res.*, 105(B4), 8229-8242.
- 579 Paterson, M. S. (1982) The determination of hydroxyl by infrared-absorption in quartz,
580 silicate-glasses and similar materials, *Bull. Mineral.*, 105, 20-29.
- 581 Ralph, R.L., L.W. Finger (1982) A computer program for refinement crystal orientation
582 matrix and lattice constants from diffractometer data with lattice symmetry constrains.
583 *Journal of Applied Crystallography*, 15, 537–539.
- 584 Romano, C., B.T. Poe, J. Tyburczy, and F. Nestola (2009) Electrical conductivity of
585 hydrous wadsleyite, *Eur. J. Mineral.*, 21, 1615-622.

- 586 Samara, G.A. (1984) High-pressure studies of ionic conductivity in solids. In:
587 Ehrenreich, H., D. Turnbull, eds., Solid State Physics, Advances in Research and
588 Applications, vol. 38. Academic Press, London, pp. 1-80.
- 589 Schock, R.N., A.G. Duba, and T.J. Shankland (1989) Electrical conduction in olivine. J.
590 Geophys. Res., 94, 5829-5839.
- 591 Shankland, T.J. and A.G. Duba (1990) Standard electrical conductivity of isotropic,
592 homogeneous olivine in the temperature range 1100-1500°C. Geophys. J. Int., 103, 25-
593 31.
- 594 Simpson, F. (2002), Intensity and direction of lattice-preferred orientation of olivine:
595 Are electrical and seismic anisotropies of the Australian mantle reconcilable? Earth
596 Planet. Sci. Lett., 203, 535–547.
- 597 Smyth, J.R., D.J. Frost, F. Nestola, C.M. Holl, and G. Bromiley (2006) Olivine
598 hydration in the deep upper mantle: Effects of temperature and silica activity. Geophys.
599 Res. Lett., 33, L15301.
- 600 Tarits, P., S. Hautot, and F. Perrier (2004) Water in the mantle: Results from electrical
601 conductivity beneath the French Alps, Geophys. Res. Lett., 31, L06612, doi:
602 10.1029/2003GL019277.
- 603 Wanamaker, B. J., and A. G. Duba (1993), Electrical conductivity of San Carlos olivine
604 along [100] under oxygen- and pyroxene-buffered conditions and implications for
605 defect equilibria, J. Geophys. Res., 98, 489– 500.
- 606 Wang, D. J., M. Mookherjee, X. S. Xu, and S. Karato (2006) The effect of water on the
607 electrical conductivity of olivine, Nature, 443, 977-980.

- 608 Xu, Y., T. J. Shankland, and A. G. Duba (2000), Pressure effect on electrical
609 conductivity of mantle olivine, *Phys. Earth Planet. Inter.*, 118, 149– 161.
- 610 Yoshino, T., M. Takuya, S. Yamashita, and T. Katsura (2006) Hydrous olivine unable
611 to account for conductivity anomaly at the top of the asthenosphere, *Nature*, 443, 973-
612 976.
- 613 Yoshino, T., G. Manthilake, T. Matsuzaki, and T. Katsura (2008) Dry mantle transition
614 zone inferred from the conductivity of wadsleyite and ringwoodite, *Nature* 451, 326-
615 329.
- 616 Yoshino, T., T. Matsuzaki, A. Shatskiy, and T. Katsura (2009) The effect of water on
617 the electrical conductivity of olivine aggregates and its implications for the electrical
618 structure of the upper mantle. *Earth and Planetary Science Letters* 288, 291-300.

619 FIGURE CAPTIONS

620 FIG. 1 Polarized FTIR spectra of a hydrous olivine single crystal with H₂O content of
621 2215 wt ppm.

622

623 FIG. 2 Representative complex impedance spectra of a hydrous olivine single crystal at
624 8 GPa and temperatures ranging from 500 to 700 °C.

625

626 FIG. 3 Electrical conductivity of olivine at 8 GPa along different crystallographic
627 directions at various concentrations of dissolved H₂O (wt ppm). Black dashed lines are
628 reproduced from Yoshino et al., 2006. Solid red lines are Arrhenian fits (Eq. 1) through
629 the data for nominally anhydrous olivine. Solid green and blue lines are fits of Eq. 2
630 through the data for hydrous olivine conductivities.

631

632 FIG. 4 Variation of forsterite lattice parameters as a function of pressure up to 6.7 GPa
633 at room temperature from single crystal x-ray diffraction.

634

635 FIG. 5 Electrical anisotropy given as the difference between $\log \sigma_{\max}$ and $\log \sigma_{\min}$ as a
636 function of temperature for dry, 100 ppm and 1000 ppm wt H₂O.

637

638 FIG. 6 Geometric mean electrical conductivity (see Eq. 4) as a function of H₂O
639 concentration and temperatures: (a) from this study, compared to (b) Yoshino et al.
640 (2009) for polycrystalline hydrous olivine aggregates. The thick dashed lines indicate
641 the conditions at which proton conductivity and small polaron conductivity are equal as
642 a function of H₂O concentration, with small polaron conduction dominating at high T
643 and low [H₂O].

FIG. 1

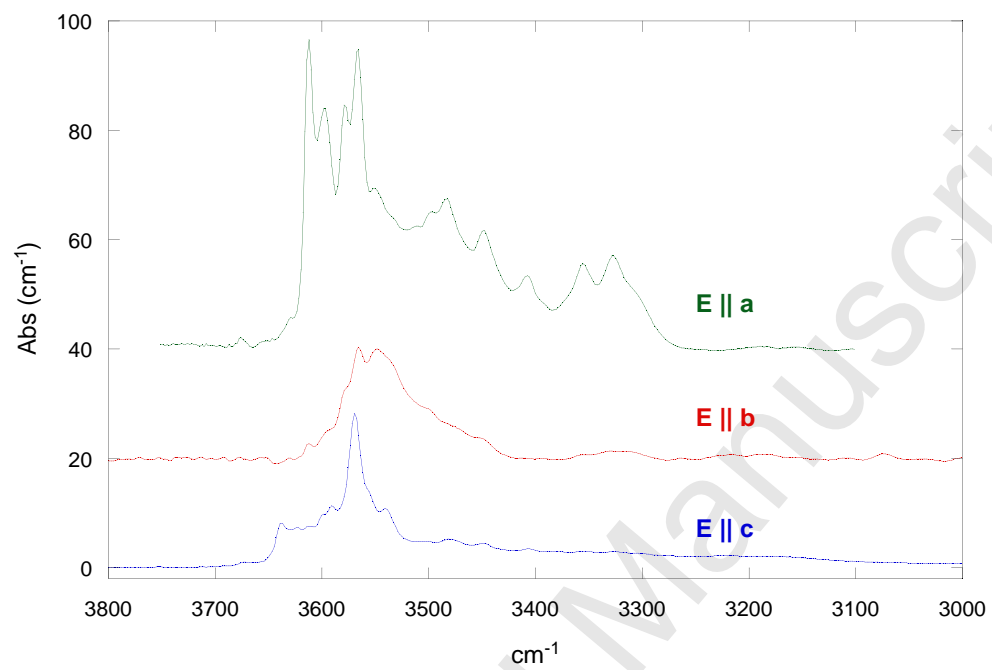


FIG. 2

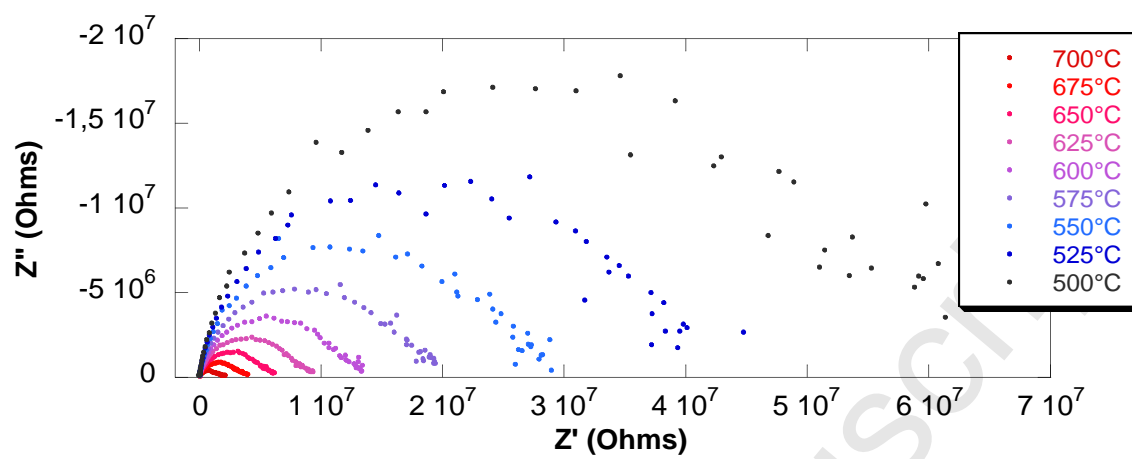


FIG. 3

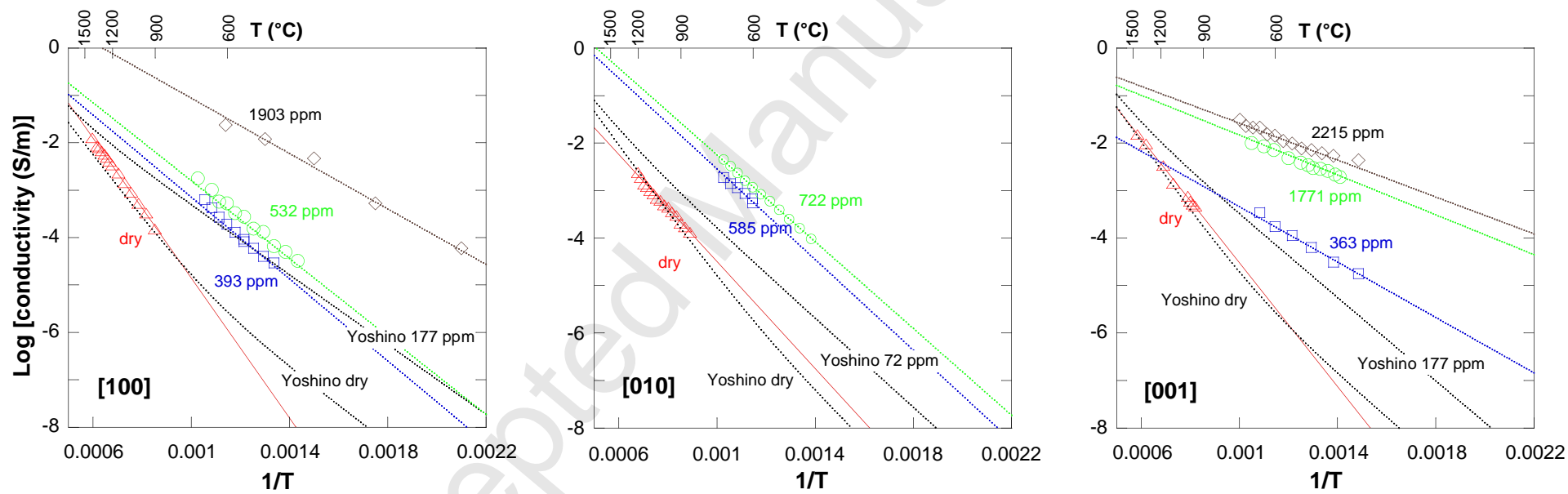


FIG. 4

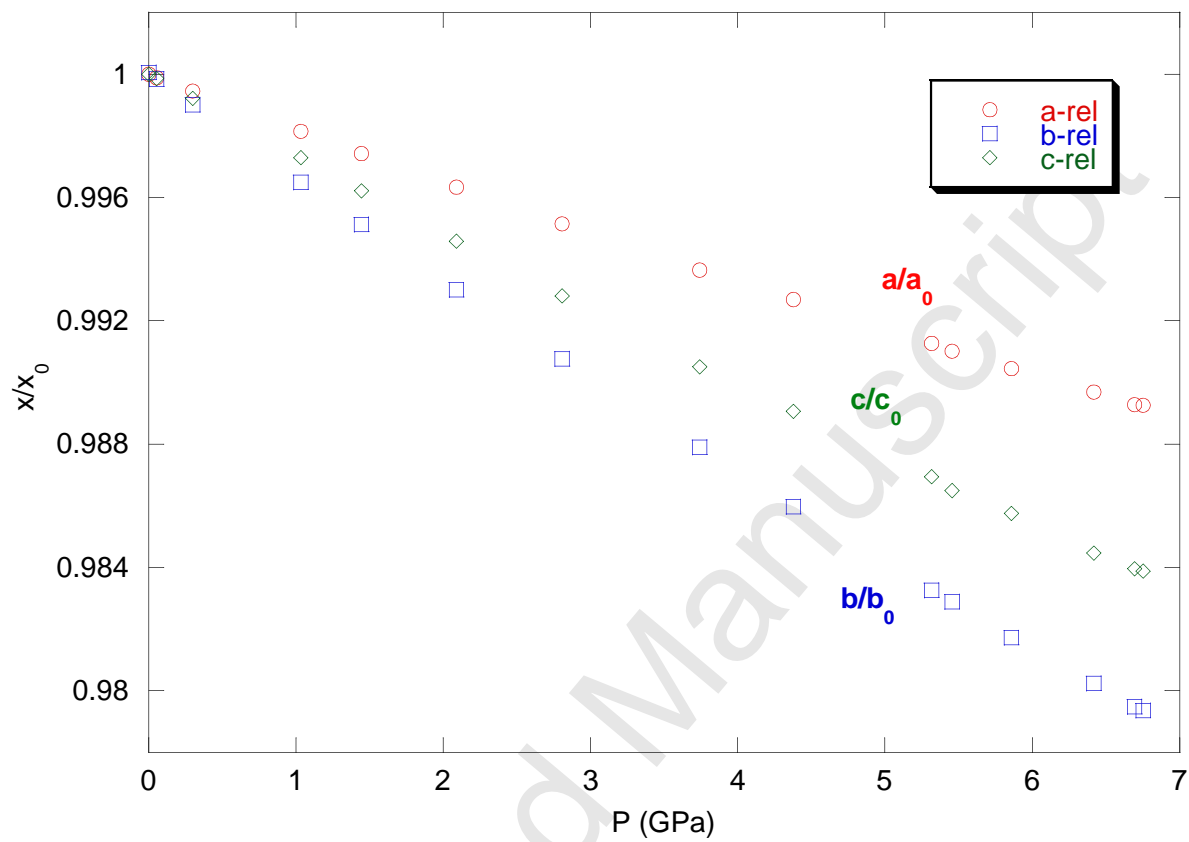


FIG. 5

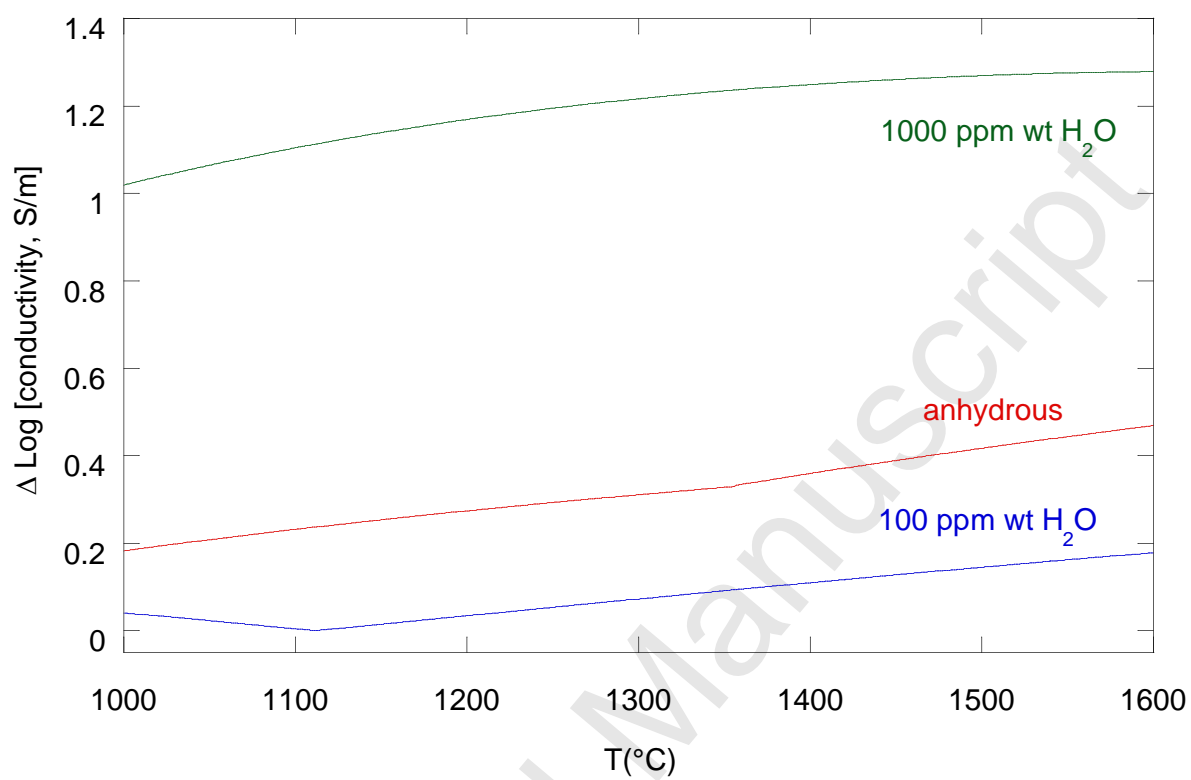


Fig. 6

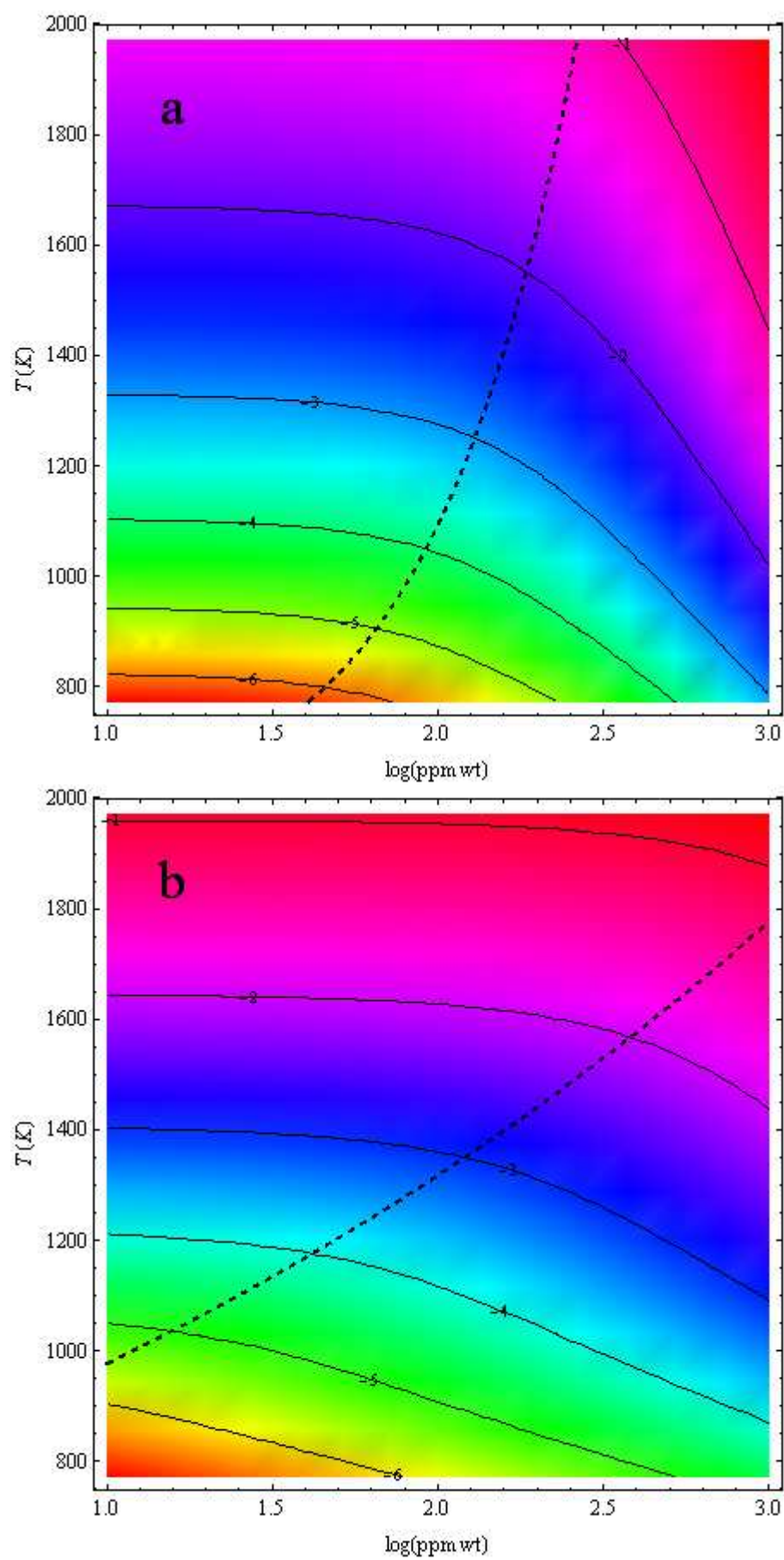


Table 1. Fitting parameters of Arrhenius equation (Eq. 1) to experimental data (8 GPa). Linear correlation coefficient R is also given to indicate goodness of fit. Standard error in H₂O analyses by FTIR is given in parentheses.

expt	orient.	[H ₂ O] wt. ppm	σ_0 (S/m)	H (eV)	R
H2329	[100]	nom. dry	334	1.46	0.9992
H2474	[100]	393(71)	57.2	0.944	0.9952
H2473	[100]	532(85)	41.1	0.851	0.9958
H2320	[100]	1903(230)	48.1	0.555	0.9939
H2476	[010]	nom. dry	13.8	1.12	0.9964
H2480	[010]	585(62)	33.1	0.819	0.9883
H2477	[010]	722(65)	247	0.919	0.9996
H2328	[001]	nom. dry	99.0	1.29	0.9982
H2472	[001]	363(52)	0.802	0.628	0.9963
H2324	[001]	1771(220)	1.37	0.401	0.9962
S3740	[001]	2215(260)	1.70	0.340	0.9824
G.M. dry			77.0	1.29	
Yoshino	[100]	nom. dry		1.35	
Yoshino	[010]	nom. dry		1.42	
Yoshino	[001]	nom. dry		1.47	

Table 2. Unit-cell parameters at different pressures of forsterite studied in this work. Standard error in last digit shown in parentheses.

P (GPa)	a (Å)	b Å	c (Å)	V (Å ³)
0.00010(1)	4.7602(1)	10.2155(1)	5.9874(3)	291.15(1)
0.055(3)	4.7596(1)	10.2135(1)	5.9866(3)	291.02(1)
0.298(2)	4.7576(1)	10.2048(1)	5.9827(2)	290.46(1)
1.035(3)	4.7514(1)	10.1792(1)	5.9712(3)	288.80(1)
1.445(3)	4.7480(1)	10.1651(1)	5.9648(3)	287.88(1)
2.091(4)	4.7428(1)	10.1436(1)	5.9550(3)	286.49(2)
2.809(4)	4.7371(2)	10.1206(2)	5.9444(4)	284.99(2)
3.741(4)	4.7299(2)	10.0915(2)	5.9306(4)	283.08(2)
4.376(5)	4.7254(1)	10.0717(2)	5.9220(4)	281.85(2)
5.316(6)	4.7187(1)	10.0440(2)	5.9092(4)	280.06(2)
*5.454(7)	4.7174(1)	10.0402(3)	5.9065(7)	279.75(4)
5.859(6)	4.7147(1)	10.0284(2)	5.9021(6)	279.06(3)
6.417(7)	4.7111(1)	10.0131(3)	5.8944(8)	278.06(4)
6.696(6)	4.7092(3)	10.0054(4)	5.8914(9)	277.59(5)
6.750(7)	4.7091(5)	10.0042(6)	5.8909(14)	277.52(7)
Notes: *data measured during decompression				

Table 3. Best fit parameters for hydrous olivine conduction. Standard error shown in parentheses.

Chi-squared values are also shown as an indication of goodness of fit.

$\sigma = \sigma_0 C_w \exp\left(\frac{-H - \alpha C_w^{1/3}}{kT}\right)$				
orientation	σ_0	H(eV)	α	χ^2
100	$3.86(1.36) \times 10^{-2}$	1.26(0.04)	$-5.49(0.20) \times 10^{-2}$	0.21
010	0.290(0.061)	1.50(0.05)	$-6.64(0.50) \times 10^{-2}$	0.013
001	$1.04(0.22) \times 10^{-3}$	0.812(0.016)	$-3.27(0.07) \times 10^{-2}$	0.079
$\sigma = \sigma_0 C_w^r \exp\left(\frac{-H}{kT}\right)$ (from Wang et al., 2006)				
orientation	σ_0	H(eV)	r	χ^2
100	$3.53(3.72) \times 10^{-10}$	0.628(0.044)	3.55(0.20)	0.95
010	$2.59(2.60) \times 10^{-8}$	0.911(0.014)	3.47(0.16)	0.010
001	$1.70(1.03) \times 10^{-9}$	0.440(0.026)	2.53(0.06)	0.24