Electrical conductivity anisotropy of dry and hydrous olivine at 8 GPa

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

Abstract

The effects of dissolved H2O on the electrical conductivity and its anisotropy in olivine (Fo90) at 8 GPa were investigated by complex impedance spectroscopy. At nominally anhydrous conditions, conduction along [1 0 0] and [0 0 1] is slightly higher than along [0 1 0] in contrast to observations made at lower pressures in earlier studies. Increasing H2O content increases conductivities but activation energies are lower and H2O concentration dependent. The use of polarized FTIR spectroscopy to determine H2O concentrations reveals a weaker than expected effect that water has on olivine conductivity and distinguishes our results from earlier studies based on analyses using non-polarized infrared spectroscopy. We show that at H2O concentrations of a few hundred wt ppm or less, that the dominant conduction mechanism at mantle temperatures between 1000–1500◦C is proton hopping along [1 0 0]. Increasing H2O content increases conductivities but activation energies are lower and H2O concentration dependent. The use of polarized FTIR spectroscopy to determine H2O concentrations reveals a weaker than expected effect that water has on olivine conductivity and distinguishes our results from earlier studies based on analyses using non-polarized infrared spectroscopy. We show that at H2O concentrations of a few hundred wt ppm or less, that the dominant conduction mechanism at mantle temperatures between 1000–1500◦C is proton hopping along [1 0 0]. Additionally, at 1000 wt ppm and 1500◦C, an isotropic conductivity derived from the data is about 1 order of magnitude greater than that for nominally anhydrous olivine. Thus, in regions of the mantle characterized by anomalously high conductivities and both electrical and seismic anisotropy, significant amounts of dissolved hydrogen can be expected.

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tory conductivity data of nominally anhydrous minerals and EM profiles generated from magnetotelluric observations. Hydrogen diffusion in olivine is faster than the mobility of intrinsic defects (Kohlstedt and Mackwell, 1998), such that estimated conductivities of hydrous olivine through a proton conduction mechanism are in better accord with upper mantle conductivity (Karato, 1990) and electrical anisotropy (Evans et al., 2005). Wang et al. (2006) measured hydrous polycrystalline olivine conductivity at 4 GPa and concluded that 80 wt ppm H2O in olivine would increase its conductivity by more than a factor of 10 at 1400 °C and account for the generally high conductivity of the oceanic asthenosphere. In contrast, Yoshino et al. (2006) concluded that extrapolation of their data to higher temperatures does not increase conductivity enough to explain the observed bulk conductivity of the upper mantle. Yoshino et al. (2006), however, did not determine how conductivity varies with varying water content along any of the three crystallographic directions, but rather assumed that conductivity increased linearly with H2O concentration without change in activation energy. In a later study, Yoshino et al. (2009) carried out additional experiments on hydrous polycrystalline aggregates of olivine and determined the H2O concentration dependence.

In this study, we investigate the electrical properties of single crystal San Carlos olivine (Fo90) as a function of dissolved H2O content at 8 GPa using complex impedance spectroscopy in a multianvil apparatus. We find that the higher pressure of this study has a profound influence on electrical anisotropy compared to studies at lower pressure, particularly for the case of hydrous olivine. We also find that significantly greater concentrations of H2O in olivine (ca. 1000 ppm) are required to increase olivine conductivity by a factor of 10 at upper mantle temperatures. In order to couple the conductivity data with the elastic properties of olivine we have also investigated in situ high-pressure an anhydrous synthetic forsterite by single-crystal X-ray diffraction using a diamond-anvil cell.

## 2. Experimental methods

### 2.1. Hydration of olivine single crystals

Oriented single crystals of San Carlos olivine (Fo90) were machined into 1.8 mm dia. × 2 mm cylinders and placed in welded Pt capsules (2.0 mm o.d.) sandwiched between a mixture of fine-grained synthetic talc (Mg3Si4O10(OH)2) and brucite (Mg3(OH)6) powder (2.0 mm o.d.) to form a hydrous polycrystalline inform. The design of the conductivity cell is described in detail by Poe and Xu (1999). The presence of a cylindrical Mo foil shield lined with a small amount of polyolefin powder is a key component of the cell. The shield is placed between sample and furnace primarily to minimize interference between the higher 50 Hz voltage applied to operate the furnace and the variable frequency signal applied across the electrodes to measure complex impedance. Additionally, the shield is grounded in common with the furnace to eliminate current leakage along the outer surface of the sample and also serves as a foil buffer according to the Mo + O2 = MoO2 equilibrium. Both Wang et al. (2006) and Yoshino et al. (2006) used Ni/NiO to buffer their lower pressure experiments, whereas Yoshino et al. (2009) also used Mo/MoO2 to buffer their 10 GPa experiments. Measurements were made with a Solartron 1260 Impedance/Gainphase analyzer operating at 1.0 V amplitude and frequencies from 102 to 10–1 Hz. A typical measurement consisted of heating to a maximum temperature, depending on volatile content, and repeatedly acquiring the complex impedance spectrum every 10–15 min until it remained unchanged (on the order of 1 h). Subsequent spectra were taken upon decreasing temperature only in order to maintain the sample’s H2O concentration measured post-run in light of possible dehydration at the maximum temperature of the measurement.

Expt Expt Orient. [H2O] wt ppm \( \sigma_0 \) (S/m) \( H \) (eV) \( \varepsilon \)
--- --- --- --- --- --- --- --- ---
H2329 [1 0 0] Nom. dry 334 1.46 0.9992
H2474 [1 0 0] 393(71) 57.2 0.944 0.9952
H2473 [1 0 0] 532(83) 41.1 0.851 0.9958
H2320 [1 0 0] 1903(230) 48.1 0.555 0.9939
H2476 [0 1 0] Nom. dry 13.8 1.12 0.9964
H2480 [0 1 0] 585(62) 33.1 0.819 0.9883
H2477 [0 1 0] 722(65) 247 0.919 0.9996
H2328 [0 0 1] Nom. dry 99.0 1.29 0.9982
H2472 [0 0 1] 363(52) 0.802 0.628 0.9963
H2324 [0 0 1] 1771(220) 1.37 0.401 0.9962
S3740 [0 0 1] 2215(260) 1.70 0.340 0.9824
G.M. dry 77.0 1.29
Yoshino [1 0 0] Nom. dry 1.35
Yoshino [0 1 0] Nom. dry 1.42
Yoshino [0 0 1] Nom. dry 1.47

### 2.2. Complex impedance spectroscopy

Complex impedances were measured at 8 GPa in either a 1000-tonne or 1200-tonne Kawai-type multianvil apparatus using 11 mm truncation edge length tungsten carbide anvils and 18 mm edge length MgO octahedra. The design of the conductivity cell is described in detail by Poe and Xu (1999). The presence of a cylindrical Mo foil shield lined with a small amount of polyolefin powder is a key component of the cell. The shield is placed between sample and furnace primarily to minimize interference between the higher 50 Hz voltage applied to operate the furnace and the variable frequency signal applied across the electrodes to measure complex impedance. Additionally, the shield is grounded in common with the furnace to eliminate current leakage along the outer surface of the sample and also serves as a foil buffer according to the Mo + O2 = MoO2 equilibrium. Both Wang et al. (2006) and Yoshino et al. (2006) used Ni/NiO to buffer their lower pressure experiments, whereas Yoshino et al. (2009) also used Mo/MoO2 to buffer their 10 GPa experiments. Measurements were made with a Solartron 1260 Impedance/Gainphase analyzer operating at 1.0 V amplitude and frequencies from 102 to 10–1 Hz. A typical measurement consisted of heating to a maximum temperature, depending on volatile content, and repeatedly acquiring the complex impedance spectrum every 10–15 min until it remained unchanged (on the order of 1 h). Subsequent spectra were taken upon decreasing temperature only in order to maintain the sample’s H2O concentration measured post-run in light of possible dehydration at the maximum temperature of the measurement. It is quite likely that for the more H2O-rich samples, partial dehydration occurred at the maximum temperature (Yoshino et al., 2006). However, afterwards, at lower temperatures, observed Arhenian behavior would suggest a negligible amount of additional dehydration. The complex impedance data were fit to an expression for an RC parallel equivalent circuit, allowing for some deviation (≤10%) of the circle center from the real axis. From the determined resistance and the sample and electrode dimensions, electrical conductivity was determined. Experimental error, arising mainly from uncertainties in the sample dimensions and any non-ideality of the form of the data with respect to the equivalent circuit, is estimated to be about 5% relative.

### 2.3. Polarized FTIR spectroscopy

Samples recovered after complex impedance spectroscopy were analyzed by polarized infrared spectroscopy using a Bruker IFS 120 HR high resolution Fourier-transform spectrometer and IR microscope with Cassegrainian optics. The concentration of dissolved H2O in olivine was determined using the calibration of Bell et al. (2003) who showed that the calibration of Paterson (1982) for unpolarized FTIR spectra may underestimate water content in olivine by a factor of 2–4 owing to the extreme IR pleochroism of olivine. Table 1 lists H2O concentrations (in wt ppm) for samples after complex impedance measurements. Similar to previous observations (Mosenfelder et al., 2006; Smyth et al., 2006; Kohlstedt et al., 1996) for laboratory-synthesized H2O-rich samples, multiple absorption bands in the range 3300–3500 cm–1 are observed in addition to the main peaks between 3500 and 3600 cm–1.

### 2.4. Single-crystal XRD

In order to better understand how differences in electrical conductivity might be related to structural changes to the crystal lattice at these conditions, we also performed a series of single-crystal X-ray diffraction measurements. A colorless single crystal

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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.
of pure forsterite, free of twins and inclusions, was synthesized at room pressure and 1600 °C. Although the chemical composition of the crystal was slightly different to those of the electrical measurements, we assume that the general behavior observed can be useful to our interpretation of the conductivity results. The crystal, with dimensions 80 µm × 60 µm × 50 µm, was loaded in a BGI-type diamond-anvil cell (DAC) with T301 steel foil gasket. A mixture of methanol:ethanol (4:1) served as pressure-transmitting medium. A quartz crystal was added as an internal pressure standard (Angel et al., 1997). Unit-cell parameters (Table 1) were determined at 19 different pressures up to about 6.8 GPa and room temperature on a Huber four-circle diffractometer (non-monochromatized Mo Kα radiation) using eight-position centering of not less than 20–22 Bragg reflections according to the procedure of King and Finger (1979). Centering procedures and vector-least-square refinement of the unit-cell constants were performed using the SINGLE04 software (Angel et al., 2001) according to the protocols of Ralph and Finger (1982) without any symmetry constraints in order to monitor possible high-pressure phase transformations. The unit-cell parameters data at each pressure are reported in Table 1.

3. Results and discussion

3.1. Hydrogen incorporation in olivine

The solubility of hydrogen in olivine is low compared to its higher pressure polymorphs wadsleyite and ringwoodite (Kohlstedt et al., 1996). However, recent studies that utilized polarized FTIR spectroscopy have shown that H₂O solubility in olivine is higher by as much or more than a factor of two compared to previous studies that used non-polarized FTIR spectroscopy (Bell et al., 2003; Mosenfelder et al., 2006). An example of our polarized FTIR spectra is shown in Fig. 1 for the H₂O-rich sample S3740. Absorption is strongest with the electric field gradient, E, oriented parallel to the a-axis, consistent with the observations of previous studies (Kohlstedt et al., 1996; Bell et al., 2003; Mosenfelder et al., 2006). Also, similar to Kohlstedt et al. (1996) we observe several strong absorption bands at lower OH stretching frequencies (3300–3500 cm⁻¹) in our synthetically hydrated samples which do not appear in the spectra of natural olivine samples having much lower H₂O concentrations (Mosenfelder et al., 2006). Differences between the spectra of synthetically hydrated and natural olivine specimens illustrate that hydrogen incorporation in olivine is a complex function of oxygen fugacity and silica activity in addition to water fugacity (Mosenfelder et al., 2006). The pressure of the hydration experiments varied from 3 to 8 GPa in order to vary water fugacity and resulted in a range of H₂O concentrations from 363 to 2215 wt ppm (see Table 1), based on the calibration of Bell et al. (2003) for polarized FTIR spectra. Interestingly, in earlier attempts to hydrate single crystals of olivine using a piston cylinder apparatus (up to 3 GPa) the recovered run products were often opaque and/or fractured such they could not be used for conductivity measurements. Uncertainties in the effect of H₂O on conductivity are primarily related to these analyses, however, as spectra could be obtained only post-electrical measurement in order to preserve sample geometry and orientation for determination of its conductivity. Additional sources of error in the H₂O concentrations stem from inhomogeneities revealed upon reducing the size of the aperture (<ca. 600 µm²) and uncertainties in baseline subtraction owing to spectra composed of very broad and overlapping absorption bands.

3.2. Complex impedance spectra

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

Conductivities are shown for each crystallographic direction at anhydrous and various concentrations of dissolved H₂O in Fig. 3. For each individual sample log conductivity decreases linearly with reciprocal temperature according to the Arrhenius expression:

\[ \sigma = \sigma_0 \exp \left( -\frac{H}{kT} \right) \]  

where \( k \) is the Boltzmann constant, \( T \) is the absolute temperature and log \( \sigma_0 \) and \( H \) are the intercept and slope, respectively, of the linear regressions. Best-fit values of the pre-exponential term \( \sigma_0 \) and the activation enthalpy \( H \) for each experiment are listed in Table 2 along with crystallographic orientation and measured H₂O concentration. Because the correlation of the data to Eq. (1) is very high.
in all cases, we have assumed that H₂O concentration during the electrical measurement remained constant and equal to that of the post-measurement FTIR analysis of the sample. Although it is not observed here, non-Arrhenian behavior would likely be the result of either a change in chemical composition during the measurement, such as loss of dissolved H₂O, or from a temperature dependent change in the conductivity mechanism. In the former case, such behavior would be irreversible with temperature, whereas in the latter case, we can expect the behavior to be reversible and characterized by a stronger temperature dependence (higher H) at lower 1/T.

3.3. Electrical conductivity of dry olivine

For the anhydrous samples, conductivities were determined at temperatures ranging from 850 to 1436 °C, overlapping both the small polaron and Mg vacancy conduction regimes expected as the dominant charge transport mechanisms at low and high temperatures, respectively at 1 atm (Schock et al., 1989; Hirsch et al., 1993; Constable and Roberts, 1997; Du Frane et al., 2005). Also shown in Fig. 3 are the results of Yoshino et al. (2006) obtained at 3 GPa, in comparison to those at 8 GPa reported by Yoshino et al. (2009) for dry polycrystalline olivine at 10 GPa. However, they report that Yoshino et al. (2009) did observe ionic conduction in their dry polycrystalline olivine at 10 GPa. In this case, such behavior would be irreversible with temperature, whereas in the latter case, we can expect the behavior to be reversible and characterized by a stronger temperature dependence (higher H) at lower 1/T.

![Fig. 3. Electrical conductivity of olivine at 8 GPa along different crystallographic directions at various concentrations of dissolved H₂O (wt ppm). Black dashed lines are reproduced from Yoshino et al. (2006). Solid red lines are Arrhenian fits (Eq. (1)) through the data for nominally anhydrous olivine. Solid green and blue lines are fits of Eq. (2) through the data for hydrous olivine conductivities. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)](image)

The lower pressure studies of both Schock et al. (1989) and Yoshino et al. (2006) indicate that conduction along [100] is lower compared to one or both of the other crystallographic directions. Despite the seemingly good agreement illustrated in Fig. 3 between our data and those of Yoshino et al. (2006) at anhydrous conditions, at 8 GPa and 1200 °C we find that conduction along [100] and [001] are about equal and approximately 0.2 log units higher compared to [010]. This difference can be attributed to the small, but distinct changes in activation enthalpy from 3 to 8 GPa along each crystallographic axis. While the activation enthalpy for conduction along [100] remains high, it is reduced along both [010] and [001] in comparison to those at 3 GPa reported by Yoshino et al. (2006). A reduction in activation enthalpy with increasing pressure, here for the case of small polaron conduction, can be explained by decreasing interatomic distances between Fe²⁺ and Fe³⁺, which facilitate the electron hole hopping mechanism.

Results from our single crystal diffraction measurements of forsterite up to 6.7 GPa indicate that the [1 0 0] direction is the least compressible of the three axes, in good agreement with other recent in situ single-crystal X-ray diffraction studies (Liu and Lee, 2006; Katsura et al., 2009) and with resonant ultrasonic spectroscopy (Isaak et al., 1989). At high pressure, interatomic distances would thus be shortened more along both the b and c directions compared to the a direction (Fig. 4). A more rapidly changing cell parameter is likely to be accompanied by a greater change in activation energy for conduction in that direction. Thus, at 8 GPa and the higher temperatures associated with the deeper upper mantle, conductivity along [100] becomes higher than [010], opposite to that which

![Table 2](image)

Table 2

<table>
<thead>
<tr>
<th>P (GPa)</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>V (Å³)</th>
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<td>5.9874(3)</td>
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<td>10.0042(6)</td>
<td>5.8909(14)</td>
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</table>

* Data measured during decompression.
is observed at ambient pressure (Schock et al., 1989) and at 3 GPa (Yoshino et al., 2006).

For dry olivine conductivity anisotropy remains relatively weak because of the minor changes in temperature dependence from 3 to 8 GPa. However, the higher conductivity along [1 0 0] presents important implications where both electrical and seismic anisotropy are observed in the upper mantle. Because both high conductivities and fast shear wave velocities cannot be rationalized by LPO in dry olivine at shallow depths (<3 GPa), the presence of dissolved H2O in olivine has been suggested as responsible for favoring conduction along [1 0 0] via a fast proton conduction mechanism (Evans et al., 2005). Based on our data at 8 GPa corresponding to greater depths (>200 km), proton diffusion is not required to justify a higher conductivity along [1 0 0] and the observed electrical anisotropy at these depths, such as below the North Central craton of Australia (Simpson, 2002). Because the effects of pressure and temperature on the electrical conductivity of dry olivine are different along each crystallographic direction, electrical anisotropy changes with depth in the mantle without requiring the presence of dissolved hydrogen to invoke a different conduction mechanism. The absence of an ionic conduction pathway at 8 GPa may also contribute to the difference in anisotropy that is observed at 3 GPa (Yoshino et al., 2006). We also stress that this conclusion can be drawn independently of our conductivity results for hydrous olivine which are discussed below (Section 3.4), and therefore is not compromised by the additional experimental uncertainties due to analyses of H2O content nor by long extrapolations of those data to the higher temperatures associated with the mantle.

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

3.4. Hydrous olivine conductivity

For the hydrous olivine samples, temperatures did not exceed 700 °C during the measurement in order to minimize possible dehydration of the sample. We cannot exclude the possibility that the dominant conduction mechanism in hydrous olivine changes at temperatures above 700 °C. However, Wang et al. (2006) measured the conductivity of polycrystalline hydrous olivine at temperatures as high as 1000 °C and determined an activation enthalpy of 87 kJ/mol (ca. 0.9 eV), significantly lower than that for dry olivine conduction and similar to the activation enthalpies observed in this study at lower H2O concentrations (see Table 2).

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

$$\sigma = \sigma_0 C_W \exp \left( -\frac{H - aC_W^{1/3}}{kT} \right)$$

In the case of hydrous olivine, Yoshino et al. (2006, 2009) and Wang et al. (2006) also determined their H2O concentrations using FTIR spectroscopy, but all according to the calibration of Paterson (1982) for non-polarized spectra. Our H2O determinations are based on the calibration of polarized FTIR spectra by Bell et al. (2003), who demonstrated its importance for pleochroic minerals. Mosenfelder et al. (2006) recently pointed out that use of the Paterson calibration for determining dissolved H2O concentrations in Fe-bearing olivine can underestimate concentrations by as much as a factor of 4 compared to its determination by the calibration of Bell et al. (2003). The use of a different FTIR calibration may contribute to the differences in the effect of dissolved H2O on the conductivity of olivine in our study compared to the study of Yoshino et al. (2006). If the H2O concentrations from Yoshino et al. (2006) were underestimated due to their use of the Paterson calibration, then the effect of dissolved H2O on olivine conductivity that they report would be overestimated by a similar factor.

We have chosen to fit the hydrous olivine data separately from the anhydrous data based on two observations upon examination of Fig. 3 and Table 2. Most importantly, individual datasets show strongly Arrhenian behavior, which allows us to assume that a single charge transport process dominates each sample’s electrical conductivity. Slight changes in slope are detectable only in the case of conduction along [1 0 0] at the lowest H2O concentration and along [0 0 1] at the highest H2O concentration (Fig. 3). Because we do not observe any systematic occurrence, rather than indicating a change in conduction mechanism, this behavior may be related to some form of experimental factor, such as insufficient time allowed for sample re-equilibration at lower temperatures. Secondly, activation enthalpies are clearly lower and most likely H2O concentration dependent for the hydrous olivine data. This latter observation suggests that the dominant mechanism in hydrous olivine cannot be the same as that for anhydrous olivine.

Our fits of Eq. (2) to the hydrous olivine conductivity data for each of the three crystallographic orientations are also illustrated in Fig. 3. We note that within experimental error, these H2O concentration dependent approximations are in excellent agreement...
with the simple Arrhenian fits to each individual dataset. Best-fit parameters are listed in Table 3. Also shown in Fig. 3 are the approximations reported by Yoshino et al. (2006) for dry and [H2O]-

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.

<table>
<thead>
<tr>
<th>Orientation</th>
<th>$\sigma_0$ (S/m)</th>
<th>$H$ (eV)</th>
<th>$\alpha$</th>
<th>$\chi^2$</th>
</tr>
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<tbody>
<tr>
<td>0 0 1</td>
<td>3.86(1.36) $\times 10^{-2}$</td>
<td>1.26(0.04)</td>
<td>5.49(0.20) $\times 10^{-2}$</td>
<td>0.21</td>
</tr>
<tr>
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<td>1.50(0.05)</td>
<td>6.64(0.50) $\times 10^{-2}$</td>
<td>0.013</td>
</tr>
<tr>
<td>0 0 1</td>
<td>1.04(0.22) $\times 10^{-3}$</td>
<td>0.812(0.016)</td>
<td>3.27(0.07) $\times 10^{-2}$</td>
<td>0.079</td>
</tr>
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</table>

sigma = $\sigma_0 C_{H2O} \exp \left( \frac{H}{RT} \right)$

from Wang et al. (2006)

We also fit the equation used by Wang et al. (2006) to our data for hydrous olivine. The form of the equation and results from those fits are also given in Table 3. Similar to Eq. (2), the pre-exponential term is concentration dependent, but includes two adjustable parameters, $\sigma_0$ and $r$. Here we find that the $\sigma_0$ term returns a very large relative error. Additionally, the higher $\chi^2$ values from this fit compared to the using Eq. (2) are the result of a fixed rather than $H_2O$ concentration dependent activation enthalpy, even though the total number of adjustable parameters is the same for both fits. Interestingly, the best-fit values for the exponent $r$ (from about 2.5 along [1 0 0] to 3.5 along [0 1 0] and [0 0 1]) are much higher than that determined by Wang et al. (2006) for hydrous polycrystalline olivine (Ca. 0.6). As Wang et al. (2006) discussed, the value of $r$ is indicative of the type of defect mechanism that controls proton hopping. Romano et al. (2009) measured the electrical conductivity of hydrous wadsleyite and determined a best-fit value of $r = 1.44$ using the same equation. As stated previously, the higher temperature measurements of Wang et al. (2006) may explain some of the differences from our study as the mechanism for conduction may change with increasing temperature. Indeed, Wang et al. (2006) assumed that both small polaron and proton hopping conduction mechanisms contributed to the bulk conductivity at high temperature, such that the fits to their data included both a dry (small polaron) component and a wet (proton hopping) component. However, it is clear that at lower temperatures, the temperature dependence for conductivity is strongly coupled to dissolved water content in olivine such that $H_2O$ (Eq. (2) provides a much more robust approximation of the experimental data.

3.5. Important differences from previous studies

A comparison of our results to those from Wang et al. (2006) and Yoshino et al. (2006) is made difficult because of the pressure effects that are likely to play a role between 3 and 8 GPa. Regardless of such effects, however, neither Wang et al. (2006) nor Yoshino et al. (2006) demonstrate any link between temperature dependence of conductivity and $H_2O$ concentration. Our results show that activation enthalpy decreases with increasing water concentration. This observation not only indicates that the proton hopping mechanism becomes less important at higher temperatures as small polaron conduction begins to dominate, but also that the effect of dissolved water diminishes with increasing temperature. Yoshino et al. (2009) later investigated the effect of water concentration at 10 GPa, but on polycrystalline olivine aggregates. Their study, like ours, observes small polaron conduction to temperatures above 1700 K in nominally anhydrous samples. Similar to our results, Yoshino et al. (2009) show that activation enthalpy decreases with increasing $H_2O$ content, but their dependence ($\alpha$ term, Table 3) is less than what is observed here. The reason for this difference is still unclear as the pressures and temperatures of both studies are quite similar. The major differences in the experimental approach are that Yoshino et al. (2009) used polycrystalline samples, non-polarized FTIR spectroscopy and a corresponding FTIR calibration by Paterson (1982) whereas our study examined single crystal samples, and determined $H_2O$ contents using polarized FTIR and calibration by Bell et al. (2003).

The fit to Eq. (2) allows us to determine electrical anisotropy, given simply by the difference between $\log \sigma_{\text{max}}$ and $\log \sigma_{\text{min}}$ among the three different crystallographic directions as a function of temperature, shown for nominally anhydrous olivine and at $H_2O$ concentrations of 100 and 1000 wt ppm in Fig. 5. We can justify extrapolation of the hydrous data to higher temperatures as the conductivities remain higher than those for dry olivine, except in the case of [0 0 1] above 1350°C at the lowest $H_2O$ concentration (see Fig. 3). No extrapolations are made for dry olivine for which electrical anisotropy is determined using the fit parameters to the Arrhenius expression (Table 2). For both anhydrous olivine and at 100 ppm $H_2O$, conduction along [1 0 0] remains highest. Interestingly, at 100 wt ppm $H_2O$, electrical conductivity is more isotropic than that of dry olivine. However, at 1000 wt ppm $H_2O$, electrical anisotropy is greater, by about a factor of 10 along [0 1 0]
Fig. 5. Electrical anisotropy given as the difference between \( \log \sigma_{\text{max}} \) and \( \log \sigma_{\text{min}} \) as a function of temperature for dry, 100 ppm and 1000 ppm wt H\(_2\)O.

compared to the [001] direction. At these H\(_2\)O rich conditions, anisotropy is nearly independent of temperature. The complex behavior we observe over this range of H\(_2\)O content could be related to the speciation of H\(_2\)O in olivine as a function of its concentration, which is still poorly understood at present. Hushur et al. (2009) report that the high-pressure hydration mechanism in forsterite is principally M1 site vacancy with the proton on the O1–O2 edge shared between M1 octahedra. This mechanism would increase c-axis compressibility and facilitate proton movement along the edge-sharing M1 octahedral chains parallel to c. We would then expect a lower activation enthalpy along c compared to b for conduction dominated by proton hopping (see Table 3) much like what we observe for the anhydrous case of small polaron hopping where b-axis compressibility is greatest (Fig. 4) and its activation enthalpy lowest (Table 2). This would of course influence its anisotropy but in a different manner compared to anhydrous olivine or H\(_2\)O-poor olivine for which the dominant conduction mechanism may be unrelated to the presence of hydrogen (see below Section 3.6).

3.6. Competing charge transport mechanisms

It is important to note that the anhydrous data are not included in the fit to Eq. (2) because the conduction process cannot involve a protonated charge carrier. Even at low H\(_2\)O concentrations, the activation enthalpy is lower than that for anhydrous olivine, such that at higher temperatures it would be expected to intersect the anhydrous data. This suggests that electrical conduction in hydrous olivine is dominated by a proton-bearing charge carrier at low temperatures but crosses over to the small polaron conduction mechanism at a temperature that depends on the H\(_2\)O concentration. By combining the results of the fits to Eq. (2) for hydrous olivine with the best-fit parameters to the Arrhenius equation for the anhydrous data, we can determine the temperature of this crossover for the total geometric mean electrical conductivity, which is equal to the sum of the small polaron (\( \sigma_{\text{Fe}} \)) and proton (\( \sigma_{\text{H}} \)) geometric mean conductivities:

\[
\sigma = \left( \sigma_{\text{Fe}001} \sigma_{\text{Fe}100} \sigma_{\text{Fe}010} \right)^{1/3} + \left( \sigma_{\text{H}001} \sigma_{\text{H}100} \sigma_{\text{H}010} \right)^{1/3}
\]

Fig. 6a illustrates the variation of \( \log \sigma \) with H\(_2\)O concentration and temperature and the boundary between the small polaron dominant and H-bearing dominant fields. The crossover temperature indicated by the dashed black line increases smoothly with log[H\(_2\)O]. We find that the slope of the boundary is quite steep due to the large change in activation energy with increasing H\(_2\)O content. At H\(_2\)O concentrations below a few hundred wt ppm, the dominant charge transport mechanism is that of small polarons.

Fig. 6b shows similar behavior using the results of Yoshino et al. (2009). At the far left of the plot beginning at 10 wt ppm H\(_2\)O, which corresponds to small polaron conduction, the two models are in very good agreement. Only at the highest temperatures, at which Yoshino et al. (2009) observe ionic conduction, do the nominally anhydrous conductivities begin to diverge. For hydrous olivine, our results show that the strong H\(_2\)O concentration dependence of the crossover temperature implies that significant concentrations of dissolved H\(_2\)O (several hundred wt ppm) could cause the mantle to switch from small polaron to proton hopping conduction. The results from Yoshino et al. (2009), however, would indicate this to be less likely due to a weaker H\(_2\)O concentration dependence. We have assumed that the effect of H\(_2\)O on the small polaron mechanism has a negligible effect on the anhydrous conductivity simply because we have no conductivity data for hydrous olivine at sufficiently high temperatures that might be suggestive of a different conduction mechanism. However, it is likely that dissolved H\(_2\)O in olivine also influences the small polaron conductivity indirectly.
through its effect on the $\text{FeO}_2$ via autodissociation:

$$\text{H}_2\text{O} = \text{H}_2 + 1/2\text{O}_2$$  \hspace{1cm} (4)

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

4. Conclusions

As mentioned above, with increasing temperature the effect of $\text{H}_2\text{O}$ concentration diminishes. However at 1500 °C, the calculated isotropic conductivity (geometric mean) at 1000 ppm $\text{H}_2\text{O}$ remains a factor of 10 higher than that for nominally anhydrous olivine. We conclude that in the deeper half of the upper mantle, both the absolute conductivity and electrical anisotropy of $\text{H}_2\text{O}$-bearing olivine can indeed account for observed magnetotelluric signatures.

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