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Toward a unified hydrous olivine electrical conductivity law

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Abstract It has long been proposed that water incorporation in olivine has dramatic effects on the upper mantle properties, affecting large-scale geodynamics, and triggering high electrical conductivity. But the laboratory-based laws of olivine electrical conductivity predict contrasting effects of water, precluding the interpretation of geophysical data in term of mantle hydration. We review the experimental measurements of hydrous olivine conductivity and conclude that most of data are consistent when errors in samples water contents are considered. We report a new law calibrated on the largest database of measurements on hydrous olivine oriented single crystals and polycrystals. It fits most of measurements within uncertainties, and is compatible with most of geophysical data within petrological constraints on mantle olivine hydration. The conductivity anisotropy of hydrous olivine might be higher than dry olivine, but preferential orientation should produce moderate anisotropy (~0–0.8 log unit). In the oceanic mantle, the enhancement of olivine conductivity is limited to ~1 log unit in the maximum range of mantle olivine water concentrations (0–500 wt ppm). Strongest enhancements are expected in colder regions, like cratonic lithospheres and subduction settings. High conductivities in melt-free mantle require great depths and high water concentrations in olivine (>0.1 S/m at >250 km and >200 wt ppm). Thus, the hydration of olivine appears unlikely to produce the highest conductivities of the upper mantle.

1. Introduction

The interpretation of high electrical conductivities is a key step in the understanding of the global geodynamics in the upper mantle. The enhancement of upper mantle conductivities due to the incorporation of trace amounts of hydrogen in olivine, the dominant upper mantle phase, has been the most influencing hypothesis [Karato, 1990] with important geodynamics implications [Hirth and Kohlstedt, 1996, 2003; Ingrin and Skogby, 2000; Bergovici and Karato, 2003; Tarits et al., 2004; Evans et al., 2005; Simpson and Tommasi, 2005; Khan and Shankland, 2012]. In particular, olivine hydration has also been suggested to generate electrical anisotropy due to preferential orientations related to deformation and stress distribution in the lithosphere and the upper asthenosphere [Evans et al., 2005; Simpson and Tommasi, 2005].

Although this hypothesis has been proposed in 1990 [Karato, 1990], the first experimental characterizations of the effect of water on olivine conductivity have been published 16 years later by Wang et al. [2006] and Yoshino et al. [2006]. Other experimental measurements have completed the data set [Yoshino et al., 2009; Poe et al., 2010; Yang, 2012; Dai and Karato, 2014a, 2014b] but the laws derived from these studies predict contrasted conductivities [Wang et al., 2006; Yoshino et al., 2009; Poe et al., 2010; Jones et al., 2012], precluding any unequivocal interpretation of electrical conductivities in the upper mantle in terms of mantle hydration (Figure 1a). Much of the debate has focused on the incompatibility of the laws of Wang et al. [2006] and Yoshino et al. [2009] as they predict the most contrasted conductivities, differing by up to 2 log unit. Indeed, while the former concluded to a strong enhancement of olivine conductivity by minute amounts of water, the latter concluded to a negligible effect at mantle temperatures.

The different groups calibrated their conductivity laws on their own experimental data, probably because of the apparent incompatibility between the different studies. The recent work by Jones et al. [2012] was the first attempt of reconciliation. The authors propose a combination of the
previous laws with a recalibration of some of the key parameters based on conductivity-water content in xenoliths data from the South African craton. The approach by Jones et al. [2012] relies on two geophysical observations, and is not based on the analysis of the global experimental database itself.

The inconsistencies between the laboratory studies have essentially been attributed to the various conductivity measurement protocols, however those generally produce uncertainties of about 10–20% only [Yoshino et al., 2008, Appendix A]. On the other hand, the concentration of water in the olivine samples are commonly uncertain by several tens of percent and are biased by up to a factor of ~4 when the infrared (IR) calibration of Paterson [1982] is used for polycrystals [e.g., Bell et al., 2003] (Figure 1b and Appendix Table A1). The concentration of water in olivine is certainly the less well-constrained experimental parameter but was poorly discussed so far, precluding the rigorous test and the whole treatment of the database (note that, in accordance with most studies, the term “water” does not refer to molecular water but to structurally bounded hydrogen (OH groups), which is commonly measured as equivalent H$_2$O concentration).

Here, we propose that most of the discrepancies between the conductivity laws derive from the experimental uncertainties and biases on the water concentration of the olivine samples. We perform a global analysis of the existing experimental data in order (i) to test the internal consistency of the database and (ii) to adjust a simple empirical law on the largest data set which can be used for geophysical purpose. We propose a new law which calculates the electrical conductivity and anisotropy of olivine as a function of its water content.

2. Consistency of the Experimental Database

The published conductivity measurements on oriented single crystals of hydrous olivine cover wide ranges of water concentration (0–2200 wt ppm) and temperature (200–1440 °C) [Yoshino et al., 2006; Poe et al., 2010; Yang, 2012]. The inspection of the run conditions reveals that water content is definitely the experimental parameter having the largest uncertainties, reaching typically several tens of percent (Figure 1b and Appendix Table A1). When these uncertainties are considered, the conductivities collected on single crystals...
do form a consistent data set, following a single global trend over the whole range of H$_2$O concentration (Figure 1b).

The isotropic conductivities collected on hydrous olivine polycrystals by Wang et al. [2006] and Dai and Karato [2014a, 2014b] also compare fairly well with this trend (Figure 1b). These three studies provide consistent data with values slightly higher than the trend of the oriented single crystal data. This mostly results from the use of the IR calibration of Paterson [1982] on olivine polycrystals which is known to underestimate water concentrations by a factor of $\sim$2–4, depending on the samples and the analytical conditions [Bell et al., 2003; Mosenfelder et al., 2006a; Dai and Karato, 2009; Withers et al., 2012]. Up to several tens of percent of hydrogen in the samples of Wang et al. [2006] and Dai and Karato [2014a, 2014b] is in the form of molecular water, probably in fluid inclusions or in the intergranular medium, as illustrated by the broad band centered at 3400 cm$^{-1}$ superposed to the OH bands on their IR spectra [e.g., Mosenfelder et al., 2006b]. Unless this water exsolved from olivine structure during decompression at the end of the runs, it leads to overestimate the concentration of structural hydrogen available for conduction enhancement (note, however, that Wang et al. [2006] partially subtracted it; see their Supplementary Information 2). Therefore, the water concentrations of the polycrystals of Wang et al. [2006] and Dai and Karato [2014a, 2014b] have to be corrected by an unknown factor which may vary from one sample to the other, but which should be less than $\sim$4. When this additional source of error is considered (right-hand side of the error bars in Figure 1b), the data of Wang et al. [2006] and Dai and Karato [2014a, 2014b] are undistinguishable from the data obtained on oriented single crystals, and merge with the global trend.

Dai and Karato [2014a, 2014b] investigated the effect of pressure and oxygen fugacity on the conductivity of hydrous olivine. Increasing both parameters decreases conductivity, but to a small extent only. Over the experimental temperature range (600–1000°C), increasing pressure from 4 to 10 GPa and oxygen fugacity from Mo/MoO$_2$ to Re/ReO$_2$ buffer decreases conductivity by 0.1–0.3 and 0.3–0.4 log unit, respectively (see also Appendix Figure A1). Note that the change in oxygen fugacity from Mo/MoO$_2$ to Re/ReO$_2$ buffer is much greater than the variations expected for the Earth’s upper mantle based on petrological surveys [Frost and McCammon, 2008]. The effect of pressure on hydrous olivine is similar to that on dry olivine, where conductivity decreases by $\sim$0.3 log unit from 4 to 10 GPa at 1000°C [Xu et al., 2000; Dai et al., 2010]. In contrast the effect of oxygen fugacity on hydrous olivine is opposite, since dry olivine conductivity increases by $\sim$0.4 log unit from Mo/MoO$_2$ to Ni/NI buffer at 1000°C [Dai et al., 2010]. The change in sign of the oxygen fugacity dependence between dry and hydrous olivine implies that the dependence is weak at intermediate water concentrations (the samples of Dai and Karato [2014b] contained 180–280 wt ppm H$_2$O according to the calibration of Paterson [1982]) and even vanishes at a given C$_{H_2O}$. Thus, pressure and oxygen fugacity appears to be parameters of secondary importance, and the electrical conductivity of olivine is mainly correlated to its water content, as can readily be appreciated from the comparison between the various studies (Figure 1b).

The measurements on hydrous olivine polycrystals of Yoshino et al. [2009] lay about 1 log unit below the data from the other studies (Figure 1b). Obviously, this gap cannot result from the underestimation of water concentration due to the IR calibration of Paterson [1982] as this should shift their data further away from the other studies (Figure 1b). It is not likely attributable to the iron content in their samples (Fo91–92.5) since it is similar to the other studies (Appendix Table A1). As discussed above, it cannot result from differences either in pressure or in oxygen fugacity as these parameters have small effects. For instance, the data of Yoshino et al. [2009] are up to almost 2 log unit lower than those of Poe et al. [2010] while they were collected at almost the same conditions (10 versus 8 GPa, identical Mo/MoO$_2$ buffer). The origin of the discrepancy between the data of Yoshino et al. [2009] and the rest of the database is unknown: does it result from a different and unidentified experimental condition, or from a bias? It should be mentioned that there is an internal inconsistency in the water contents of the samples reported in their original paper. In their Table 1, the water contents expressed as wt % are, after conversion, $\sim$10 times higher than those expressed as H/10$^6$Si. Using the water contents expressed in the latter unit shifts their data on the same trend as the others, but the authors recently clarified that the values reported as wt % are the correct ones [Yoshino et al., 2014]. Nevertheless, the 50 wt ppm H$_2$O reported for their driest sample (SK1055) is largely overestimated since no OH bands are visible on the IR spectrum of this sample, while they are clearly apparent on the spectrum of the sample containing $\sim$100 wt
Table 1. Parameters of the Best Fit Law (Equation (1)) and its Misfits With Experimental Data (Given as Mean Absolute Deviations (MAD) Between the Decimal Logarithm Of Modeled and Experimental Conductivities)\(^a\)

<table>
<thead>
<tr>
<th>Orientation</th>
<th>(\Delta H_{\text{Vacancy}}) (kJ/mol)</th>
<th>(\log n_{\text{Vacancy}}) ((\sigma) in S/m)</th>
<th>(\Delta H_{\text{Polaron}}) (kJ/mol)</th>
<th>(\log n_{\text{Polaron}}) ((\sigma) in S/m)</th>
<th>(\Delta H_{\text{Hydrous}}) (kJ/mol)</th>
<th>(\log n_{\text{Hydrous}}) ((\sigma) in S/m/wt ppm)</th>
<th>(\alpha) (kJ/mol/wt ppm(^{1/3}))</th>
<th>MAD Misfit (log unit)</th>
</tr>
</thead>
<tbody>
<tr>
<td>// [100]</td>
<td>261 ± 48</td>
<td>5.92 ± 1.99</td>
<td>146 ± 27</td>
<td>2.19 ± 1.09</td>
<td>92 ± 9</td>
<td>-1.48 ± 0.57</td>
<td>2.56 ± 0.59</td>
<td>-1.28 ± 0.57</td>
</tr>
<tr>
<td>// [010]</td>
<td>268 ± 55</td>
<td>5.45 ± 2.07</td>
<td>141 ± 21</td>
<td>2.38 ± 1.10</td>
<td>95 ± 13</td>
<td>-0.70 ± 0.09</td>
<td>0.88 ± 0.09</td>
<td>-0.51 ± 0.09</td>
</tr>
<tr>
<td>// [001]</td>
<td>234 ± 47</td>
<td>4.67 ± 1.94</td>
<td>146 ± 24</td>
<td>2.51 ± 1.06</td>
<td>81 ± 9</td>
<td>-1.97 ± 0.09</td>
<td>1.94 ± 0.54</td>
<td>-1.77 ± 0.09</td>
</tr>
<tr>
<td>Isotropic</td>
<td>239 ± 46</td>
<td>5.07 ± 1.32</td>
<td>144 ± 16</td>
<td>2.34 ± 0.67</td>
<td>89 ± 7</td>
<td>-1.37 ± 0.45</td>
<td>1.79 ± 0.47</td>
<td>-1.17 ± 0.45</td>
</tr>
</tbody>
</table>

\(\alpha\) The overall MAD misfit with the database is 0.07 log unit. Two sets of \(n_{\text{Hydrous}}\) and \(\alpha\) are reported depending on whether water concentrations from the calibration of Bell et al. [2003] or from that of Withers et al. [2012] have to be used (the latter law should be preferred when inverting conductivities for obtaining more realistic water concentrations). The isotropic conductivity is reported in the form of equation (1) for sake of simplicity (with a MAD < 0.01 log unit, this fit negligibly deviates from exact geometric average). Errors on individual parameters are given as \(2\sigma\) (see Figure 3 for uncertainties on predicted isotropic conductivity and conductivity anisotropy).

3. The New Conductivity Law

Our purpose is to provide a law for geophysical purpose which unifies the largest part of the database. The approach remains empirical since, as we shall see later, the conduction mechanisms in hydrous olivine remain unclear.

We consider the conductivity data from all published experimental measurements on single crystals and polycrystals of hydrous olivine [Yoshino et al., 2006; Wang et al., 2006; Poe et al., 2010; Yang, 2012; Dai and Karato, 2014a, 2014b]. Additional data from experiments performed under nominally dry conditions are also included to improve accuracy at low water contents and high temperature [Xu et al., 2006, 2009; Dai et al., 2010]. As discussed above, the data of Yoshino et al. [2009] are not included, except for the high temperature part (>1400°C) of the measurements on their nominally dry sample (SK1223). The database regroups 287 conductivity measurements on 38 samples with temperatures and water concentrations ranging over 200–1727°C and 0–2200 wt ppm (details on data selection can be found in Appendix A and Table A1).

For the sake of simplicity, pressure and oxygen fugacity dependences are not parameterized since, as mentioned above, the effect of these parameters on the conductivity of olivine appears to be minor compared to that of water concentration. The database compiles experiments performed between 1 and 10 GPa and with Mo/MoO\(_2\) or Ni/NiO buffer in almost equal proportion, so our law is roughly representative of mean upper mantle pressure and oxygen fugacity conditions.

We consider the superposition of three conductive processes

\[
\sigma = \sigma_0 \text{Vacancy} e^{-\Delta H_{\text{Vacancy}}/RT} + \sigma_0 \text{Polaron} e^{-\Delta H_{\text{Polaron}}/RT} + \sigma_0 \text{Hydrous} C_{\text{H2O}} e^{-\Delta H_{\text{Hydrous}}/RT} \alpha^{1/3} \text{ppm}^{1/3},
\]

where \(R\) is the gas constant, \(T\) the absolute temperature, \(C_{\text{H2O}}\) the concentration of water in olivine, and the \(\sigma_0\)s and the \(\Delta Hs\) the preexponential factors and activation enthalpies, respectively. The two first terms represent electrical conduction in anhydrous olivine, which is controlled by small polaron hopping from ferrous to ferric ions and, at high temperature, by the diffusion of cation vacancies [Schöck et al., 1989; Wannamaker and Duba, 1993; Xu et al., 2000; Constable, 2006; Yoshino et al., 2009; Dai et al., 2010]. The third term corresponds to the electrical conduction related to the introduction of hydrogen species. It was applied to conduction in hydrous olivine in order to account, through the positive parameter \(\alpha\), for the decrease of activation enthalpy as a function of water concentration evidenced in the studies where water concentration was varied over wide ranges [Yoshino et al., 2006, 2009; Poe et al., 2010].
Equation (1) was adjusted on the single crystals data for each of the three axes ($\sigma_{[100]}$, $\sigma_{[010]}$, $\sigma_{[001]}$) along with the geometric mean which was adjusted to polycrystals data

$$\sigma_{\text{isotropic}} = \sqrt[3]{\sigma_{[100]} \sigma_{[010]} \sigma_{[001]}}. \quad (2)$$

Thus, our law is composed of four equations, i.e., one for each crystallographic axis, allowing addressing conductivity anisotropy, and one for isotropic conductivity, relevant to olivine aggregates without preferential orientation. At each iteration of the optimizing procedure, the three sets of $\sigma_0$, $\Delta H_s$, and $x$ from $\sigma_{[100]}$, $\sigma_{[010]}$, and $\sigma_{[001]}$ are changed and the geometric mean $\sigma_{\text{isotropic}}$ is generated, so that the overall misfit with the whole database (mean absolute deviations MAD), from both single crystals and polycrystals, is minimized. The key feature of the modelling is that, for each sample, the water concentration is optimized by allowing it to vary within the confidence intervals on the measurements, and optimized values are labeled on the curves (see also Appendix Table A1). DK14a: Dai and Karato [2014a]; DK14b: Dai and Karato [2014b]; DLLHS10: Dai et al. [2010]; PRNS10: Poe et al. [2010]; WMXK06: Wang et al. [2006]; XSD00: Xu et al. [2000]; Y12: Yang [2012]; YMSK09: Yoshino et al. [2009]; YMYK06: Yoshino et al. [2006].
parameters and on predicted conductivities are calculated as twice the standard deviation of those yielded by the 20,000 simulations.

The results of the best fit law are reported in Figure 2 and in Table 1 (see also Table A1 for optimized water concentrations). The mean absolute deviations with single crystals data are 0.05–0.08 log unit and 0.10 log unit with polycrystals data, corresponding to an overall MAD of 0.07 log unit, which is comparable to the uncertainties on conductivity measurements. The 0.08 and 0.13 log unit MAD with the data acquired at various pressures and oxygen fugacities by Dai and Karato [2014a, 2014b], respectively, shows that neglecting these parameters only introduces small biases (Appendix Figure A1). Our optimization yields water contents 2.4 times higher on average than those given by Wang et al. [2006] and Dai and Karato [2014a, 2014b] for hydrous polycrystals (Appendix Table A1), which falls in the range of correction factors for the calibration of Paterson [1982] (i.e., ~2–4) [Bell et al., 2003; Mosenfelder et al., 2006a; Dai and Karato, 2009; Withers et al., 2012]. The deviation from the highest correction factors may represent the fraction of hydrogen trapped as molecular water in fluid inclusions which did not contribute to conductivity enhancement. These results confirm that the database is consistent, and is reproduced by a simple law with good accuracy. Including all
the polycrystals data of Yoshino et al. [2009] strongly lowers the quality of the fit for both single crystals and polycrystals data, with an overall MAD increased by a factor ~3 (0.23 versus 0.07 log unit; Table A2), confirming that these data for hydrous conduction seem incompatible with the rest of the database.

Withers et al. [2012] reported a new IR calibration which corrects the water concentrations of the calibration of Bell et al. [2003] by a factor of ~2/3 (100 wt ppm H2O according to Withers et al. [2012] = 158 wt ppm H2O according to Bell et al. [2003]). As modeled water concentrations are rather consistent with the calibration of Bell et al. [2003], we applied this conversion to provide a law consistent with the new calibration of Withers et al. [2012] (this changes \( \sigma^\text{Hydrous}_r \) and \( \sigma^\text{Hydrous}_m \) only, Table 1). This law should be preferred, especially when inverting conductivities into olivine hydration in order to obtain more realistic water concentrations. Therefore, unless otherwise mentioned, the water concentrations reported below will refer to the calibration of Withers et al. [2012]. We still provide a law consistent with the calibration of Bell et al. [2003] in order to facilitate comparison with previous works as this calibration was extensively used over the past decade.

The \( \Delta H^\text{Polaron} \) and \( \Delta H^\text{Polaron} \) values for isotropic conductivity are 239 ± 46 and 144 ± 16 kJ/mol, respectively, in agreement with conduction by small polaron hopping and metal vacancy diffusion in olivine [Dai et al., 2010; Xu et al., 2000; Constable, 2006; Yoshino et al., 2009; see also Chakraborty, 2010]. The \( \Delta H^\text{Hydrous} \) value is much smaller, i.e., 89 ± 7 kJ/mol for isotropic conductivity, in agreement with previous investigations on hydrous olivine [Yoshino et al., 2006; Wang et al., 2006; Yoshino et al., 2009; Poe et al., 2010; Yang, 2012; Dai and Karato, 2014a, 2014b].

Isotropic conductivity and maximum conductivity anisotropy maps as a function of temperature and water concentration are shown in Figure 3, along with propagated uncertainty maps. As expected, uncertainties are much lower in the domains where measurements were performed than in those where extrapolation is required, for instance, at high temperature and high water concentration (Figure 3). The average uncertainty on the isotropic conductivity is 0.17 log unit over the map (Figure 3b), and is identical in the more mantle-relevant, for instance, at high temperature and high water concentration (Figure 3). The average uncertainty of the maximum anisotropy on the same maps is 0.21 log unit (Figure 3c) and 0.27 log unit over the map (Figure 3d). Between 1000 and 1500°C, the mean maximum anisotropy (log \( \sigma^\text{Hydrous}_m/\sigma^\text{Hydrous}_r \)) is 0.21 ± 0.20 for 0–10 wt ppm H2O, 0.37 ± 0.27 for 10–200 wt ppm H2O, and 0.46 ± 0.34 for 200–500 wt ppm H2O. The anisotropy of hydrous olivine might be higher than that of dry olivine, but this is uncertain. In any case, the range of maximum anisotropy including uncertainty indicates that preferential orientation of olivine should produce moderate conductivity anisotropy (~0–0.8 log unit).

4. Comparison With Previous Laws

The law of Poe et al. [2010] allows the calculation of both oriented and isotropic conductivities. It yields large MADs when compared with the whole database, being 3 times larger than our law (0.21 versus 0.07 log unit; Table 2). This result is mainly due to the underestimation of the conductivities at intermediate water concentrations since these authors investigated samples with >360 wt ppm H2O (calibration of Bell et al. [2003]), except for nominally dry samples. At 1000 wt ppm H2O (calibration of Bell et al. [2003]) and between 1000 and 1600°C, the law of Poe et al. [2010] yields ~1 to 1.3 log unit maximum anisotropy (log \( \sigma^\text{Hydrous}_m/\sigma^\text{Hydrous}_r \)). Even if uncertain, the maximum anisotropy predicted by our law is much lower, being 0.30 ± 0.32 to 0.53 ± 0.38 log unit in the same conditions.

The other published laws provide isotropic conductivities only, so the comparison is restricted to measurements on polycrystals (about one quarter of the database). The MAD of our law with polycrystals data is similar to the law of Wang et al. [2006] (0.10 versus 0.11 log unit; Table 2), while most of these data come from their study and those of Dai and Karato [2014a, 2014b]. Because Wang et al. [2006] underestimated water concentrations with the IR calibration of Paterson [1982] and because they did not investigate samples with small water contents (100 wt ppm minimum; calibration of Paterson [1982]), their law overestimates the effect of water to more than 1 log unit at water concentrations below ~200 wt ppm (Figure 1b).

The law of Jones et al. [2012] has a slightly lower MAD with the polycrystals data (0.09 log unit; Table 2). However, as it is a combination of the previous laws which includes that of Wang et al. [2006], it also
overestimates the conductivities at low to intermediate concentrations, but the overestimation is attenuated (Figure 1b).

The law of Yoshino et al. [2009] largely underestimates the conductivities over the whole range of water concentration (0.68 log unit MAD with polycrystals data; Table 2) since it was calibrated on their data. Their law however remains almost parallel to the trend formed by the rest of the database (Figure 1b).

### 5. Conduction Mechanisms

It is well established that electrical conduction in anhydrous olivine is controlled by small polaron hopping from ferrous to ferric ions and diffusion of metal vacancies [Schock et al., 1989; Wanamaker and Duba, 1993; Xu et al., 2000; Constable, 2006; Yoshino et al., 2009; Dai et al., 2010]. In contrast, the mechanisms of electrical conduction in hydrous olivine, supposed to be controlled by the diffusion of hydrogen defects, remain unclear. Hydrogen is mainly incorporated as neutral defects in the cationic sublattices of olivine, i.e., as two protons in Me-site vacancies \((2H)^{\text{Me}}\) defects or as four protons at Si site vacancies \((4H)^{\text{Si}}\) defects) [e.g., Bai and Kohlstedt, 1993; Braithwaite et al., 2003; Lemaire et al., 2004; Demouchy and Mackwell, 2006; Balan et al., 2011; Otsuka and Karato, 2011; Ingrin et al., 2013]. The diffusion of these defects requires much higher activation energies than electrical conduction in hydrous olivine (~220 and ~450 kJ/mol for \((2H)^{\text{Me}}\) and \((4H)^{\text{Si}}\) respectively, versus ~90 kJ/mol) [Demouchy and Mackwell, 2006; Padrón-Navarta et al., 2014]. Furthermore, when converted using the Nernst-Einstein equation [e.g., Philibert, 1991], the diffusivities of \((2H)^{\text{Me}}\) and \((4H)^{\text{Si}}\) yield several order of magnitude lower conductivities (Figure 4). Thus, the diffusion of hydrogen defects in Me and Si sublattices do not control electrical conduction in hydrous olivine. This observation led S. Karato and collaborators to propose that conduction is controlled by minor hydrogen defects having much higher mobility, like interstitial protons produced according to the ionization reaction \((2H)^{\text{Me}} \rightarrow H^{\text{Me}} + H^+\) [e.g., Wang, 2006; Karato, 2013]. This hypothesis is supported by the study of Dai and Karato [2014b] where, contrary to dry olivine, hydrous olivine conductivity was found to be negatively correlated to oxygen fugacity. Indeed, the chemistry of hydrogen defects in olivine predicts a dependence of ionized defects concentration on oxygen fugacity under specific electroneutrality conditions [Huang et al., 2005; Kohlstedt, 2006]. However, this hypothesis remains incompatible with two major observations.

1. According to defect equilibria, the concentration of interstitial protons, and therefore the conductivity, should be proportional to \(C_{\text{H}_2O}\), where the exponent \(r\) has to be smaller than \(3/4\), depending on the electroneutrality condition [Huang et al., 2005; Kohlstedt, 2006]. Wang et al. [2006] obtained \(r = 0.62\) by fitting their data set as a whole, but this value is uncertain since it is largely scattered when their data are considered one temperature at a time, with \(r\) being greater than 1 for the data at 1000°C and even negative for the data at 800 and 900°C (see their Figure 2). Actually, when all the studies are considered, the trend over the whole range of concentrations is not compatible with \(r < 3/4\) (Figure 1b). The exponent of the trend is higher than 1 and even increases as a function of water concentration. This increase is in turn fairly well reproduced by the decrease of the activation energy as a function of water concentration from the hydrous term...
in equation (1). Note that this decrease requires a broad range of water concentrations to be evidenced, especially at high water concentration, but is rather limited over upper mantle-relevant olivine concentrations (12 kJ/mol from 0 to 200 wt ppm). Tentative fit replacing the hydrous term in equation (1) by the equation (2) of Wang et al. [2006], i.e., $a_0^{\text{Hydrous}} C_{\text{Tot}}^{\text{Hydrous}}$, is unable to reproduce the database when $r$ is forced to be smaller than $\frac{3}{4}$ (overall MAD of 0.22 log unit, Appendix Table A2). Better fits are only obtained when $r$ is free to be greater than 1; the best fit we obtained yields $r = 1.62$ for the isotropic conductivity (Appendix Table A2). It is still less accurate than our law (overall MAD of 0.11 log unit), mainly because it cannot reproduce the decrease of activation energy at high water concentration.

2. To the best of our knowledge, the fastest hydrogen diffusion in olivine was observed during the initial steps of hydration experiments by Mackwell and Kohlstedt [1990], Kohlstedt and Mackwell [1998], and Demouchy and Mackwell [2006]. This fast water incorporation was assumed to occur via the interdiffusive exchange of interstitial proton and polaron, and to be rate-controlled by slower proton diffusion. This mechanism is restricted to minute amounts of water (<5 wt ppm), and further hydrogen incorporation proceeds much more slowly into cation vacancies. However, the fast diffusion of interstitial proton still remains incompatible with the electrical conduction of hydrous olivine since it has a higher activation energy (~150 versus ~90 kJ/mol), a much higher and different anisotropy (up to more than 2 log unit, faster along [100] axis) and yields lower conductivity after conversion (Figure 4).

Thus, it is not possible to interpret the electrical conductivity of hydrous olivine in terms of hydrogen defects diffusion according to the available data. It could therefore be considered that the electrical conduction of hydrous olivine is rather electronic than ionic, as observed in many hydrogen-doped oxides [McCluskey et al., 2012]. Further comprehension of hydrogen diffusion is also required since, for example, it is unclear why the hydrogen-deuterium interdiffusive exchange in olivine [Du Frane and Tyburczy, 2012], expected to occur via the fastest mechanisms, is slower than the diffusion of interstitial proton as given by the proton-polaron exchange (Figure 4), and is ~2 order of magnitude slower in forsterite [Ingrin and Blanchard, 2006].

Improved evaluation of hydrous olivine conductivity at high mantle temperatures and high water concentrations requires further measurements in order to detect potential additional mechanisms, but preventing water release from the samples under these conditions is experimentally challenging.

6. Comparison With Geophysical Data and Implications

The recent investigations on two kimberlites fields in southern Africa, namely Jagersfontein on the Kaapvaal craton and Gibeon on the Rehoboth terrane [Jones et al., 2012], bring a unique opportunity to test our law against the conductivity of mantle regions where water concentration and temperature are well constrained. Magnetotelluric surveys reported log $\sigma$ (with $\sigma$ in S/m) of $-3.41 \pm 0.41$ and $-2.78 \pm 0.18$ at ~100 km depth, with temperature estimates of 740 ± 25 and 850 ± 25°C for the two locations, respectively [Jones et al., 2012]. Based on measurements on xenoliths from the Kaapvaal craton [Peslier et al., 2010; Baptiste et al., 2012], Jones et al. [2012] estimated that the maximum range of water concentration in olivine at ~100 km beneath Jagersfontein is 60–150 wt ppm (calibration of Bell et al. [2003]). They assumed the same range beneath Gibeon. In these settings, our law yields isotropic conductivities (log $\sigma$) ranging from $-3.92$ to $-3.20$ and from $-3.46$ to $-2.80$ for Jagersfontein and Gibeon respectively, which compare very well with the geophysical data. In comparison, the law of Wang et al. [2006] requires 8 and 16 wt ppm to reproduce the Jagersfontein and Gibeon conductivities, and more than 800 and 1200 wt ppm for the law of Yoshino et al. [2009].

Thus, our law appears to be reliable for cratonic lithosphere and should also be reliable in the other cold regions of the upper mantle, such as the mantle wedge of subduction settings. Similarly to the other laws, it predicts that the enhancement of olivine conductivity by water weakens at high temperature. This is because the contribution of anhydrous conduction increases with temperature and tends to overcome hydrous conduction at high temperature. For instance, adding 500 wt ppm H$_2$O increases the conductivity by ~2 log unit at 1000°C, but only by ~1 log unit at 1500°C (Figure 3a). Above 1300°C, conductivity in olivine containing less than 40 wt ppm H$_2$O is predicted to be dominated by the anhydrous mechanisms (Figure 3a).

We calculated hydrous olivine conductivity profiles along cratonic and oceanic geotherms (Kaapvaal craton from Jones [1988], Canadian shield (East Abitibi) from Jaupart and Mareschal [1999], 100-Ma oceanic
The concentration of water in olivine in equilibrium with oceanic mantle is estimated to be 50–200 wt ppm, and ~500 wt ppm maximum at the boundary with the transition zone according to the petrological surveys [Hirschmann et al., 2009; Ardia et al., 2012]. Typical geophysical profiles for cratons and oceans compare fairly well with the conductivities given by our law within this range [Baba et al., 2010; Evans et al., 2011; Kuvshinov and Olsen, 2006; Lizarralde et al., 1999; Neal et al., 2000; Schultz et al., 1993]. Most of the geophysical data are compatible with olivine containing less than 200 wt ppm water, in agreement with petrological predictions. This suggests that the law is also reliable at the highest temperatures of the upper mantle.

It is crucial to consider the geochemical and petrological constraints when interpreting geophysical conductivity data in term of olivine hydration. For example, while the incorporation of ~500 wt ppm H₂O in olivine...
is possible at 400 km depth, it is limited to ~200 wt ppm at 200 km and ~50 wt ppm at 100 km beneath young oceanic lithospheres [Hirschmann et al., 2009; Ardia et al., 2012]. We calculated the conductivity at the water storage capacity of olivine equilibrated in bulk rock peridotite along a ridge adiabat, that is the maximum conductivity of hydrous olivine before the onset of peridotite melting (Figure 5c; data from Hirschmann et al. [2009] for P < 5 GPa (~150 km) and from Ardia et al. [2012] for P > 5 GPa). Above this limit, the conductivities are strongly modified since partial melts are present and water is redistributed from olivine to the liquid phase [see Naif et al., 2013; Sifré et al., 2014]. Although higher water storage is allowed in colder settings, the conductivities remain always lower than those beneath ridges because of the decrease in temperature (Figure 5). Thus, water-induced high conductivities in melt-free mantle can thus be reached at high depth only (>250 km and >200 wt ppm H₂O). See section 6 for references and calculation details.

Figure 5. Conductivity of hydrous olivine in (a, b) cratonic and (c) oceanic settings for upper mantle-relevant olivine water concentrations (0–500 wt. ppm) according to our law (consistent with the calibration of Withers et al. [2012]). Most of the geophysical data are compatible with olivine containing less than 200 wt ppm water, especially at great depth, in line with petrological predictions for normal mantle hydration. The gray transparent area in (c) corresponds to conductivities which require water concentrations higher than the storage capacity of olivine in equilibrium with peridotite along a ridge adiabat, i.e., the region where dehydration melting occurs. High conductivities (>0.1 S/m) in melt-free mantle can thus be reached at high depth only (>250 km and >200 wt ppm H₂O). See section 6 for references and calculation details.
et al., 2010; Sifr et al., 2014]. Thus, the enhancement of olivine conductivity by water over mantle-relevant water concentrations can reproduce the range of normal upper mantle conductivities, but appears unlikely to produce the highest conductivities of the upper mantle.

7. Conclusions

The analysis of the measurements of hydrous olivine conductivity shows that the experimental data from laboratory studies are mostly consistent when the uncertainties and biases in the water contents of the olivine samples are considered. Our new law of hydrous olivine conductivity best reproduces the experimental database, and is compatible with most of geophysical data within petrological constraints on mantle hydration. Nevertheless, the mechanism of olivine conductivity enhancement by water remains to be determined, as it appears incompatible with the diffusion of any hydrogen defects according to the literature data. New conductivity measurements at the highest mantle-relevant temperatures and water concentrations would also be desirable, even though those are experimentally challenging.
Our law predicts that the enhancement of olivine conductivity by water is limited to $\sim 1$ log unit beneath young oceanic lithospheres for mantle-relevant olivine concentrations (0–500 wt ppm H$_2$O). Strongest enhancements are expected in the coldest regions of the upper mantle, such as cratonic lithospheres and the mantle wedge of subduction settings. Conductivity anisotropy of hydrous olivine is uncertain. It might be more than dry olivine, but is limited to $\sim 0.8$ log unit at most. Therefore, preferential orientation of olivine should produce moderate anisotropy. High conductivities in melt-free mantle can be obtained at great depth and high water concentration only (0.1 S/m requires more than 250 km depth and 200 wt ppm H$_2$O). The hydration of olivine thus appears unlikely to produce the highest conductivities of the upper mantle.

**Appendix A: Details on Data Selection and Modeling**

The conductivities of hydrous olivine oriented single crystals and polycrystals used to calibrate our law are raw experimental data as reported in the original papers, apart from the following exceptions. (i) When repeated, measurements at given temperature and water concentration were averaged. (ii) The

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Table A2. Results of Alternative Fits*

(i) Fit with equation (1) but including all the data of Yoshino et al. [2009] to the database. The quality of the fit is strongly decreased.
(ii) The hydrous term in equation (1) is replaced by equation (2) from Wang et al.'s [2006], i.e., $\log q_{\text{Hydrous}}^0 = C_1 e^{r x D_{\text{Hydrous}}^R T}$, where the exponent $r$ is forced to be smaller than 0.75. It is unable to reproduce the data. The refinements are fixed at bound $r < 0.75$ but tend to higher values. (iii) Same without constraints on $r$. Better fits are all obtained for $r > 1$, but they are still less accurate than our law. (iv) Our best fit law (equation (1)) for comparison. Misfits are reported as mean absolute deviations (MAD) between the decimal logarithm of modeled and experimental conductivities.

Our law predicts that the enhancement of olivine conductivity by water is limited to $\sim 1$ log unit beneath young oceanic lithospheres for mantle-relevant olivine concentrations (0–500 wt ppm H$_2$O). Strongest enhancements are expected in the coldest regions of the upper mantle, such as cratonic lithospheres and the mantle wedge of subduction settings. Conductivity anisotropy of hydrous olivine is uncertain. It might be more than dry olivine, but is limited to $\sim 0.8$ log unit at most. Therefore, preferential orientation of olivine should produce moderate anisotropy. High conductivities in melt-free mantle can be obtained at great depth and high water concentration only (0.1 S/m requires more than 250 km depth and 200 wt ppm H$_2$O). The hydration of olivine thus appears unlikely to produce the highest conductivities of the upper mantle.

**Appendix A: Details on Data Selection and Modeling**

The conductivities of hydrous olivine oriented single crystals and polycrystals used to calibrate our law are raw experimental data as reported in the original papers, apart from the following exceptions. (i) When repeated, measurements at given temperature and water concentration were averaged. (ii) The [001]
The influence of (a) pressure and (b) oxygen fugacity on the electrical conductivity of hydrous olivine (data acquired on polycrystals by Dai and Karato [2014a, 2014b], respectively). These parameters have a weak influence on the electrical conductivity of hydrous olivine compared to that of water, as illustrated by the small dispersion of the data around our adjustments (these data were included in our global treatment; (a) and (b) were extracted from Figure 2d). Note that in order to avoid the effects of pressure and oxygen fugacity to be adjusted by optimizing water concentrations, the measurements at 4, 7, and 10 GPa of Dai and Karato [2014a] were modeled imposing the same water concentration in the three cases, and the measurements using Mo/MoO$_2$, Ni/NiO, and Re/ReO$_2$ oxygen buffers of Dai and Karato [2014b] were modeled imposing constant ratios among the three water concentrations (see Text in Appendix A).

The confidence intervals on water concentrations in which optimization was allowed were those reported in the experimental studies, assuming nonetheless a minimum uncertainty of 15% (Table A1). For the nominally dry samples where water concentration was not measured [Xu et al., 2000; Dai et al., 2010; Poe et al., 2010], we considered 0–30 wt ppm as plausible range since initially dry samples may uptake up to a few tens of wt ppm water in high pressure devices [Yoshino et al., 2006]. As discussed in section 2, the upper limits of the confidence intervals on the water concentration of the polycrystals were multiplied by a factor of 3.5 according to Bell et al. [2003], resulting in upper limits about ~4 times higher than the mean values reported by Wang et al. [2006] and Dai and Karato [2014a, 2014b] with the calibration of Paterson [1982] (Table A1). Some additional constraints were imposed on the modelling of the data of Dai and Karato [2014a, 2014b] in order to avoid the effects of pressure and oxygen fugacity to be adjusted by optimizing water concentrations and therefore to evaluate the biases introduced by the law when these parameters
Acknowledgments

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References


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