The Effect of Water on Ionic Conductivity in Olivine

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Abstract

High-temperature ionic conductivity in olivine single crystals has been measured in the [100], [010], and [001] crystallographic orientations as a function of pressure from 2 to 10 GPa, temperature from 1450 to 2180 K, and H2O content from 20 to 580 wt. ppm using multianvil presses with in situ impedance analyses. The experimental results yield an activation energy, activation volume, and H2O content exponent of 250–405 kJ/mol, 3.2–5.3 cm3/mol, and 1.3 ± 0.2, respectively, for the high-temperature ionic conduction regime. Olivine ionic conductivity has negative pressure and positive temperature dependences and is significantly enhanced by H2O incorporation. The [001] direction is more conductive than the [100] and [010] directions. The H2O-enhanced ionic conductivity may contribute significantly to the electrical conductivity profile in the asthenosphere, especially in the regions under relatively high-temperature and low-pressure conditions.

1. Introduction

Olivine is the dominant mineral in the Earth’s upper mantle. It has been proposed that olivine has three electrical conduction mechanisms (e.g., Yoshino et al., 2009): (a) proton conduction with charges carried by protons (H1+) produced by (2H)Mg × ↔ HMg′ + H1+ owing to the small amount of H2O (protons) incorporated in the crystal structure as point defects; (b) small polaron conduction caused by hopping of electron holes (h+) between ferrous and ferric iron, that is, Fe3+ ↔ Fe2+ + h+, with h+ as the charge carrier; and (c) ionic conduction controlled by the diffusion of ions between regular sites and vacancies, A_A (site 1) + V_A (site 2) ↔ V_A (site 1) + A_A (site 2), where A_A is the regular site of element A (Mg, Fe, Si, and O) and V_A is the corresponding vacant site. Mechanism (c) is dominated by Mg (Fe) diffusion because it is by orders of magnitude faster than Si and O in olivine (Chakraborty et al., 1994; Fei et al., 2013, 2014; Fei et al., 2018a). The charge carrier of ionic conduction is specialized to vacancies on regular sites (also called vacancy conduction; e.g., Gardès et al., 2014), although protons in olivine are also ionic species. The proton, small polaron, and ionic conduction mechanisms dominate olivine conductivity at relatively low (~1200–1750 K), and high (>~1750 K) temperatures, respectively, owing to their different temperature dependences (Constable et al., 1992; Constable, 2006; Gardès et al., 2014; Yoshino et al., 2009).

To understand the electrical conductivity profiles in the upper mantle, a series of experimental studies have been performed to measure the proton and small polaron conductivities in olivine (e.g., Du Frane et al., 2005; Dai & Karato, 2014a, 2014b; Poe et al., 2010; Wang et al., 2006; Xu et al., 1998; Yang, 2012). Their results suggest that the proton conduction is significantly enhanced by water incorporation. It may account for the magnetotellurically detected anomalously high and highly anisotropic electrical conductivity (10−1–10−2 S/m) in the asthenosphere at 70–120 km depth beneath young plates near the East Pacific Rise (Baba et al., 2006; Evans et al., 2005), which cannot be explained by small polaron conductivity in dry olivine. However, this idea was later refuted (e.g., Gardès et al., 2014, 2015; Yoshino et al., 2006, 2009) because newer experimental results show that proton conductivity even in H2O-saturated olivine is insufficient to explain the highly conductive asthenosphere.

The ionic conduction mechanism, in contrast, has received only minimal attention because its contribution to olivine bulk conductivity is considered to be significant only at temperatures above 1750 K (e.g., Constable et al., 1992), which is unrealistically high for the majority of asthenosphere. However, this conclusion is based on dry olivine experiments. Incorporation of H2O produces additional point defects on Mg (Fe) sites (Demouchy & Mackwell, 2006; Kohlstedt & Mackwell, 1998) and enhances the exchange of Mg (Fe) ions between regular and vacant sites (Fei et al., 2018a, 2018b), which is expected to raise the ionic conductivity. Therefore, although the contribution of ionic conductivity is negligible in dry olivine at asthenospheric temperatures (<1750 K), it may become significant by considering small amounts of H2O in the asthenosphere.
(Fei et al., 2018a). To evaluate this hypothesis, knowledge about the H$_2$O-content dependence of olivine ionic conductivity is required. However, such experimental results have not been reported because olivine dehydration occurs at high temperatures (Yoshino et al., 2009), and the temperature range of previous H$_2$O-effect related studies was therefore limited to ~1400 K (e.g., Dai & Karato, 2014a; Wang et al., 2006; Yang, 2012), which is insufficient for observing ionic conduction.

In this study, we measured the conductivity of olivine single crystals at pressures of 2 to 10 GPa, temperatures of 1400 to 2180 K, and H$_2$O contents of ~20 to 580 wt. ppm along the [100], [010], and [001] crystallographic axes. Our results demonstrate that olivine ionic conductivity is enhanced by H$_2$O incorporation and may contribute significantly to the bulk conductivity of olivine under asthenospheric conditions.

2. Experimental and Analytical Methods

2.1. Starting Material

Three pieces of handpicked natural olivine single crystals from Pakistan with grain sizes of ~15 mm were used as the starting material. The initial H$_2$O content of the crystals was about 50 wt. ppm from infrared analysis, and the Fe/(Mg + Fe) atomic ratios were 9.0–9.5% by electron microprobe measurements. Trace element contents were reported in Gose et al. (2010). After orientation to the [100], [010], and [001] crystallographic directions using a single-crystal X-ray diffractometer, inclusion-free disks with a 1.0-mm diameter and 0.3-mm thickness were cored from the single crystals along crystallographic directions and used for the following conductivity measurements.

2.2. Multianvil Cell Assembly

Each olivine disk was sandwiched by two Mo electrodes, each of which consisted of one or two layers of Mo disks with a 1.0-mm diameter and 0.025 mm thickness. The sample was insulated by an MgO single-crystal sleeve and shielded by a Mo foil, which prevented the migration of conductive materials from the graphite furnace into the MgO insulator at high temperature. In Runs H4721 and H4745 (Table 1), small amounts of brucite powder were placed between the two Mo disks of each electrode as a H$_2$O source. The volume ratio of brucite to olivine is about 1/50, corresponding to ~6,000 wt. ppm bulk H$_2$O in olivine + brucite. A ZrO$_2$ sleeve surrounding the furnace was used as a thermal insulator. An MgO (+5 wt.% Cr$_2$O$_3$) octahedron with 18 mm edge lengths acted as a pressure medium. A pair of W$_{97}$Re$_3$-W$_{75}$Re$_{25}$ wires (D-type thermocouple) was connected to one electrode to measure the sample temperature, and another W$_{97}$Re$_3$ wire was connected to the other electrode for impedance analyses (Figure 1).

2.3. High P-T Experiments

After assembly, each cell was dried in a vacuum oven at 420 K for 24 hr, then loaded into a multianvil press and compressed to 2 or 4 GPa at room temperature using eight tungsten carbide cubes with edge lengths of 32 mm and truncated edge lengths of 11 mm. From test experiments, it was found that even with drying in the vacuum oven, some moisture remains in the pressure medium. The assembly was therefore heated to 1300 or 1500 K and maintained for a few hours until no decrease in apparent sample conductivity with time was observed. The pressure was then increased to the desired values of 2 to 10 GPa, and two to five heating-cooling cycles up to 2180 K were performed with a step of 30–100 K in each pressure stage. In each step, the sample was heated/cooled to the target temperature at a rate of ~100 K/min, followed by impedance analysis, which took 1–3 min. The duration of each heating-cooling cycle was 1–2 hr depending upon the temperature range. The assembly was quenched to room temperature by switching off the heating power and decompressed to ambient pressure over 10 hr.

As mentioned in section 1, olivine dehydration has prevented the investigation of H$_2$O dependence of conductivity at very high temperatures (Yoshino et al., 2009). Dehydration was also observed in this study: H$_2$O content ($C_{H2O}$) decreases from 50 to 20 wt. ppm after heating above 1700 K. Therefore, although the low-$C_{H2O}$ runs (~20 wt. ppm) (H471, I511, and H4674) were preformed up to 2200 K; the temperature was limited to 1700 K for higher-$C_{H2O}$ Runs (H4694, H4721, and H4745) (Table 1). To clearly observe ionic conductivity at relatively low temperatures, measurements were performed in the [010] and [001] directions, along which small polaron conductivity and ionic conductivity are the lowest and highest, respectively (Constable et al., 1992).
Table 1
Run Summary and Fitting Parameters From Equation 2

| Axis  | Run No. | Pressure (GPa) | Temperature (K) | Duration (hr) | C\textsubscript{H2O} (wt. ppm) /abs | Fe/(Mg + Fe) (%) | Log\(\sigma\)\textsubscript{ionic,0} (K•S/m) | \(E\)\textsubscript{ionic} (kJ/mol) | \(V\)\textsubscript{ionic} (cm\(^3\)/mol) | Log\(\sigma\)\textsubscript{sp,0} (S/m) | \(E\)\textsubscript{sp} (kJ/mol) | \(V\)\textsubscript{sp} (cm\(^3\)/mol) |
|-------|---------|----------------|-----------------|--------------|-------------------------------|----------------|---------------------------|--------------------------------|-----------------------------|-----------------------------|----------------|-----------------------------|
| [100] | I471    | 2, 4, 6, 8     | 1480–2080       | 11.5         | 20 (9)                       | 1.01/0.033     | 6.6 (4)                   | 11.6 (1)                       | 337 (15)                    | 4.2 (4)                    | 1.5 (2)               | 117 (13)                    | 0.5 (7)               |
| [010] | I511    | 2, 4, 6, 8     | 1400–2180       | 14.0         | 18 (9)                       | 1.01/0.018     | N.D. \(^b\)              | 13.2 (3)                       | 396 (25)                    | 3.2 (2)                    | 2.7 (2)               | 163 (25)                    | −0.2 (2)              |
| [010] | H474\(^a\) | 2, 4       | 1400–1650       | 6.0          | 580 (40)                    | 1.25/0.509     | 7.7 (8)                   | 15.8 (1)                       | 406 (3)                     | 4.9 (5)                    | 1.7 (4)               | 114 (8) \(^d\)            | −0.9 (13)             |
| [001] | H4674\(^a\) | 4, 6, 8, 10  | 1400–1660       | 6.4          | 270 (30)                    | 1.10/0.204     | 8.6 (15)                  | 10.8 (7)                       | 247 (20)                    | 5.3 (6)                    | 1.2 (1)               | 86 (33) \(^d\)            | 0.0 (8)               |
| [001] | H4694\(^a\) | 4         | 1540–1700       | 2.0          | 37 (8)                      | 1.01/0.029     | N.D. \(^b\)              | 11.4 (1)                       | 305 (9) \(^c\)             | N.D. \(^b\)              | 1.4 (1)               | 100 (8) \(^c,d\)           | N.D. \(^b\)           |

Note. Error bars represent one standard deviation in data statistics/fitting without the uncertainty of individual data points. The initial C\textsubscript{H2O} are about 50 wt. ppm for all the runs. The \(\sigma\) is the correction factor in equation 1, and abs is the maximum infrared absorbance at 3,000–4,000 cm\(^{-1}\). The data of fitting are given in the general repository, Zenodo (doi: 10.5281/zenodo.3386773). \(^a\)(Brucite was used as water source in H4745 and H4721). \(^b\)N.D.: Not determined. \(^c\)The \(E\)\textsubscript{ionic} and \(E\)\textsubscript{sp} of Run H4694 are calculated from \(E = H - PV\), where \(H\) is the activation enthalpy obtained at 4 GPa, and \(V\) is determined in H4674 and H4721. \(^d\)Owing to the H\(_2\)O-rich conditions in H4745, H4721, and H4694, the activation energy of the low-temperature conduction regime is substantially lower than in other runs; therefore, the small polaron conduction is probably masked by other mechanisms (e.g., proton conduction) as explained in the main text.
2.4. In Situ Impedance Analysis

In situ impedance analysis was performed using a Solartron 1260 Impedance/Gain Phase analyzer. In each measurement, an alternating voltage (1 V) with a frequency swept from $10^3$ to $10^2$–1 Hz with 20 steps per decade was applied to the electrodes, and the complex impedance was recorded at each frequency (Figure 2). The sample resistance $R$ was obtained by fitting the impedance spectrum to an equivalent parallel circuit with a resistor and constant phase element using the impedance analysis software, Z-View.

Conductivity ($\sigma$) under given pressure and temperature conditions was calculated from the formula $\sigma = 4L/\pi d^2R$, where $L$ and $d$ are the thickness (0.3 mm) and cross-sectional diameter (1.0 mm) of the sample, respectively (Fei et al., 2017).

The $L$ and $d$ had no distinct change (less than 5% shortening) before and after the high-pressure experiments. The background conductivity of the cell assembly was examined by Fe-free forsterite samples, whose conductivity is more than 1 order of magnitude lower than those in the olivine samples. The fitting of impedance spectrum causes negligible error on $\sigma$ (<1%). Additionally, the variation of Fe% (from 6.6% to 8.7% in Table 1) may affect the ionic conductivity in dry olivine by a maximum of ~30% in dry olivine (section 3.2). Therefore, the total uncertainty of $\sigma$ is by a maximum of 50%. This maximum uncertainty is also confirmed by the variation of data points in different heating-cooling cycles (Figure 3).

2.5. Infrared Analyses

The recovered cell assemblies were double-side polished and Fourier transform infrared (FTIR) spectroscopy analysis was performed along...
Figure 3. Example of conductivity values obtained in heating-cooling cycles. (a) Brucite-free (I511). (b) Brucite-bearing (H4745). The conductivity obtained in the first or second cooling and further heating-cooling cycles are repeatable. Only the first (or second) heating paths have slightly higher values. The repeatable data points in different heating-cooling cycles also indicate a maximum uncertainty of <50% for σ determination.
the cross sections using an unpolarized beam with a 30–60 μm diameter. Three or four infrared spectra in different regions (center and near the edge) of each sample were obtained. No essential differences in spectra were observed among the different regions, indicating homogeneous H₂O distribution (Figure 4). The H₂O contents were calculated by integration of the infrared absorptions from 3,000 to 4,000 cm⁻¹,

\[
C_{\text{H}_2\text{O}} = 3 \times \zeta \times 0.119 \times \int_{3000}^{4000} A(\nu) d\nu
\]

where \( C_{\text{H}_2\text{O}} \) is the H₂O content in wt. ppm, 0.119 is the calibration based on polarized FTIR from Withers et al. (2012), \( \zeta \) is the correction factor for unpolarized light (\( \zeta \approx 1 \) to 1.25 listed in Table 1 upon maximum absorbance (Withers, 2013)), and \( A(\nu) \) is the absorption coefficient at wavenumber \( \nu \) after background subtraction and thickness normalization to 1 cm.

Polarized FTIR on oriented crystals may give more precise \( C_{\text{H}_2\text{O}} \). In that case, however, the crystals should be polished along three crystallographic orientations, which is unfavorable here because the orientation and polishing process would damage the cross section of the assembly and prohibit any further observations. Therefore, only unpolarized FTIR spectra were measured on a single plane for each sample, which may introduce uncertainties in \( C_{\text{H}_2\text{O}} \) evaluation (see section 3.3). Additionally, different infrared calibrations yield different \( C_{\text{H}_2\text{O}} \). If using the Bell et al. (2003) calibration, the absolute values of \( C_{\text{H}_2\text{O}} \) are higher by about 50%, although the \( C_{\text{H}_2\text{O}} \)-exponent for ionic conductivity reported in this study should remain the same.

3. Results and Discussion

3.1. Dehydration or H₂O-Reabsorption During Conductivity Measurements

To investigate the \( C_{\text{H}_2\text{O}} \) dependence of olivine conductivity, it is necessary to know \( C_{\text{H}_2\text{O}} \) in the samples during conductivity measurements. However, \( C_{\text{H}_2\text{O}} \) is only measured by FTIR in the recovered samples after conductivity measurements. Because the actual \( C_{\text{H}_2\text{O}} \) during each impedance spectrum acquisition is unknown, we evaluate the dehydration during heating paths and H₂O-reabsorption during cooling paths according to the conductivity variation. It is expected that if significant dehydration had occurred continuously, the conductivity should have continuously decreased upon repeating heating-cooling cycles because the ionic conductivity is \( C_{\text{H}_2\text{O}} \)-dependent as shown later. Nevertheless, Figure 3 shows that, although the conductivity decreases in the first (and second) heating-cooling paths, changes were negligible in the later
paths. We therefore expect that olivine dehydration has occurred mostly in the first (and second) heating paths, but is insignificant in later heating-cooling paths. On the other hand, H₂O reabsorption is also unlikely to occur; otherwise, conductivity should have increased, rather than obtaining repeatable values in different heating-cooling cycles. The above evaluation of C\textsubscript{H₂O} variation relies on the extent of C\textsubscript{H₂O} that can produce measurable changes in conductivity. This is unknown because both conductivity and C\textsubscript{H₂O} are variables, and therefore insignificant dehydration during heating and H₂O reabsorption during cooling is still theoretically possible (Karato, 2019). In that case, the C\textsubscript{H₂O} under higher-temperature conditions for the ionic conduction regime would be slightly underestimated; namely, the conductivity is enhanced by less H₂O, which further supports our conclusion.

### 3.2. Microstructure and Composition of the Recovered Samples

Scanning electron microscopy (SEM) observations of recovered assemblies show that olivine and electrodes remain in a sandwiched structure (Figures 5a and 5b). Cracks are found within olivine crystals, which should be caused mechanically by compression and/or decompression. Nevertheless, even with cracks, the measured conductivity data still represent that for single crystal rather than polycrystalline because there is no recrystallization process, therefore, the crystallographic orientation should remain. This is confirmed by the experimental results which shows strong conductivity anisotropy. As expected, no melts or fluid phases are observed near the samples or within cracks for both brucite-bearing and brucite-free runs.

Electron microprobe analysis show lower Fe contents in the recovered samples (Table 1). The Fe/(Mg + Fe) ratio does not show any systematic variation along the axial cross section but clearly decreases near MgO along the radial cross section (Figures 6a and 6b). The decrease of bulk Fe content in olivine is therefore owing to Mg-Fe exchange between olivine and MgO, rather than absorption by Mo. Because the samples are radially surrounded by MgO, the vacancy concentration on Mg (Fe) site should remain constant by Mg-Fe exchange despite a slight decrease in the Fe/(Mg + Fe) ratio, and ionic conductivity should therefore be unaffected. In view of defect chemistry, the defect concentration on the Mg (Fe) site is related to Fe\textsuperscript{3+} in dry olivine with a charge balance of \([\text{Fe}^{3+}] = 2[\text{V}_\text{Mg}^\ast]\) (Kohlstedt, 2006; Stocker & Smyth, 1978). Under a given oxygen fugacity condition, the \([\text{Fe}^{3+}]/\Sigma \text{Fe}\) ratio should be fixed (Stocker & Smyth, 1978); thus, we have \([\text{V}_\text{Mg}^\ast] \propto \Sigma \text{Fe}\). The variation of Fe\% (Table 1) will have very limited effect on the ionic conductivity in dry olivine. For hydrous olivine, the \([\text{V}_\text{Mg}^\ast]\) is controlled by H₂O content and independent of \(\Sigma \text{Fe}\) (Kohlstedt, 2006; Kohlstedt & Mackwell, 1998).

### 3.3. \(P, T, C\text{H}_2\text{O}, \text{ and Crystallographic Orientation Dependences of Ionic Conductivity}

An example of the conductivity (\(\sigma\)) and temperature (\(T\)) relationship is shown in Figure 7. The slope of the \(\sigma-1/T\) curve increases with increasing temperature owing to the change of the dominant conduction mechanisms. The contribution of the proton conduction mechanism is difficult to quantify, as discussed in the supporting information. Because this study focuses on the ionic conductivity at asthenospheric temperatures, only data points at temperatures higher than 1400 K are plotted in Figure 8 and fitted to the Arrhenius equation with two terms,
\[ \sigma = \sigma_{\text{ionic}} + \sigma_{\text{sp}} = \frac{\sigma_{\text{ionic}}}{T} \exp \left( -\frac{E_{\text{ionic}} + PV_{\text{ionic}}}{RT} \right) + \sigma_{\text{sp},0} \exp \left( -\frac{E_{\text{sp}} + PV_{\text{sp}}}{RT} \right) \] (2)

where \( \sigma_0 \) is the preexponential factor, \( P \) is the pressure, \( T \) is the absolute temperature, \( R \) is the ideal gas constant, \( E \) is the activation energy, and \( V \) is the activation volume. Subscripted “ionic” and “sp” denote ionic and small polaron conduction mechanisms, respectively. The fitted parameters are listed in Table 1.

Both the \( E_{\text{ionic}} \) (250–405 kJ/mol) and \( V_{\text{ionic}} \) (3.2–5.3 cm\(^3\)/mol) determined in this study are substantially larger than those of proton conduction (<100 kJ/mol, <1 cm\(^3\)/mol) (Dai & Karato, 2014a, 2014b; Poe et al., 2010; Wang et al., 2006; Yang, 2012; Yoshino et al., 2006, 2009) and small polaron conduction (<160 kJ/mol, ~0 cm\(^3\)/mol) (Du Frane et al., 2005; Yoshino et al., 2009, 2012) and within experimental uncertainty identical to those of Mg (Fe) self-diffusion (~200–400 kJ/mol, 1.0–4.3 cm\(^3\)/mol) (Chakraborty et al., 1994; Fei et al., 2018a) (Tables 1 and 2). These comparisons confirm that the first term in equation 2 is Mg (Fe).
self-diffusion-controlled ionic conduction. Although the apparent negative pressure dependence of conductivity may theoretically be owing to continuous dehydration under increasing pressure, this possibility is highly unlikely because both the Mg self-diffusion coefficient and ionic conductivity under dry conditions (namely, no dehydration) show strong pressure dependences (Fei et al., 2018a; Yoshino et al., 2017).

Trace amounts of brucite were used as the H$_2$O source in Runs H4721 and H4745; however, there should be no melts or fluid phases to affect $\sigma_{\text{ionic}}$. This is verified by the consistent $E_{\text{ionic}}$ values obtained in brucite-bearing and brucite-free runs, that is, H4694 (no brucite, $E_{\text{ionic}} = 305(9)$ kJ/mol) and H4721 (with brucite, $E_{\text{ionic}} = 247(20)$ kJ/mol) in the [001] direction, I511 (no brucite, $E_{\text{ionic}} = 396(25)$ kJ/mol) and H4745 (with brucite, $E_{\text{ionic}} = 406(3)$ kJ/mol) in the [010] direction, and by the substantially larger activation enthalpy than those reported for fluid phase dominated conductivity (typically 30–60 kJ/mol, Gaillard et al., 2008; Sifré et al., 2014). The data obtained in H4721 and H4745 should therefore represent the conductivity of H$_2$O-bearing olivine rather than melt or fluid phases by excess H$_2$O from brucite.

The $E_{\text{ionic}}$ along the [010] axis in the high- and low-C$_{\text{H}_2}\text{O}$ runs (H4745 and I511) are essentially identical, whereas the data fitting indicates that $E_{\text{ionic}}$ along [001] may be C$_{\text{H}_2}\text{O}$-dependent (Table 1). However, the low $E_{\text{ionic}}$ in Runs H4721 and H4694 is likely owing to the relatively high small polaron conductivity along [001] (Constable et al., 1992), which leads to large uncertainties in the $E_{\text{ionic}}$ determination when the experimental temperature is relatively low.

The second term in equation 2 is suggested to be small polaron conduction because $E_{\text{sp}}$ and $V_{\text{sp}}$ are about 120–160 kJ/mol (except for the high C$_{\text{H}_2}\text{O}$ runs) and ~0 cm$^3$/mol, respectively, both of which are comparable with previously reported values (e.g., Constable et al., 1992; Yoshino et al., 2009, 2012) (Table 2). The $E_{\text{sp}}$
Table 2
Comparison of Activation Energy (E), Activation Volume (V), C_{H2O} Exponent, and Anisotropy for Ionic, Small Polaron, and Proton Conductions, and Mg Self-Diffusion in Olivine

|                   | E (kJ/mol) | V (cm^3/mol) | C_{H2O} exponent | Anisotropy                  | References                        |
|-------------------|------------|--------------|------------------|-----------------------------|-----------------------------------|
| Ionic conduction  | 220–405    | 3.2–5.3      | 1.3 ± 0.2        | [001] > [100] ≈ [010]       | This study; Yoshino et al. (2009)  |
| Mg self-diffusion | 250–400    | 1.0–4.3      | 1.2 ± 0.2        | [001] > [100] > [010]       | Chakraborty et al. (1994); Fei et al. (2018a) |
| Small polaron     | 120–160    | <1           | 0                | [001] > [100] > [010]       | This study; Yoshino et al. (2009, 2012) |
| Proton conduction | <100       | <1           | 0.6–1.0          | Inconsistent with each other | Dai and Karato (2014a, 2014b); Poe et al. (2010); Wang et al. (2006); Yang (2012); Yoshino et al. (2006; 2009) |

*a1.3 ± 0.2 is obtained by data fitting of [010] and [001] runs at 1700 K and assumed to be the same for [100].

obtained in Runs H4721, H4745, and H4694 are considerably lower (<115 kJ/mol) than others (Table 1). This might be because the temperature ranges for these runs were substantially smaller than others and the $E_{sp}$ determination therefore became less precise or because the small polaron mechanism is masked by other mechanisms (e.g., proton mechanism if it is valid).

Ionic conduction is found to be significantly anisotropic. The $\sigma_{ionic}$ along the [001] axis ($\sigma_{ionic[001]}$) is 3–5 times higher than that along the [100] and [010] axes ($\sigma_{ionic[100]}$ and $\sigma_{ionic[010]}$, respectively), that is, $\sigma_{ionic[001]} \gg \sigma_{ionic[100]} \approx \sigma_{ionic[010]}$ (Figure 8). This order is identical to that of Mg self-diffusivity ($D_{0[001]} \approx 4D_{0[100]} \approx 6D_{0[010]}$, Chakraborty et al., 1994), as well as to that of ionic conductivity at ambient pressure (Constable et al., 1992). Mg defects are primarily located on sites with $I$ symmetry (M1), and the migration distances of M1 defects are in the order of [001] ≈ [100] < [010] (longer distance means more difficult for migration, Ottolento et al., 1990; Brodholt, 1997). The anisotropy of both ionic conduction and self-diffusion can therefore be explained by the anisotropic hopping distances of defects on M1 sites (Brodholt, 1997; Constable et al., 1992).

Most importantly, olivine with ~270–580 wt. ppm H$_2$O has more than 1 order of magnitude higher conductivity than those with ~20 wt. ppm H$_2$O (Figure 8). On the basis of the simulation of the fitting parameters for the $\sigma_{ionic}$ term in Table 1, both $\sigma_{ionic[010]}$ and $\sigma_{ionic[001]}$ at 1700 K (average asthenospheric temperature beneath young plates, that is, about 1600 and 1800 K at 100 and 410 km depth, respectively, for a 5 My geotherm, Katsura et al., 2017; Turcotte & Schubert, 2002) show

$$\sigma_{ionic[hkl]} \propto (C_{H2O})^{1.3±0.2}$$ (3)

Note that the absolute bulk conductivity values obtained in different runs cannot be directly compared owing to the various contributions of the low-temperature mechanisms.

Because $\sigma_{ionic}$ has different temperature dependences in different runs, the $C_{H2O}$ exponent varies slightly with temperature during data fitting, but remain within uncertainty under the asthenospheric temperature range (i.e., ~1.5 at 1500 K and ~1.2 at 1800 K). In any case, the $C_{H2O}$ exponent remains in the range of 1.0–1.7 even though the the $C_{H2O}$ based on unpolarized FTIR analysis may have uncertainties as large as a factor of 2. The large $C_{H2O}$ dependence of ionic conductivity has therefore been demonstrated by direct measurement following our previous prediction based on Mg self-diffusivity, which has a $C_{H2O}$ exponent of 1.2 ± 0.2 (Fei et al., 2018a). This large $C_{H2O}$ exponent is expected because defect migration on Mg (Fe) sites in hydrous olivine occurs by the exchange of species among V$_{Me}^+$, (2H)Me$^+$, and MeMe$^+$, and the concentration of (2H)Me$^+$ is proportional to $C_{H2O}$ according to the hydration process of Mg sites, Mg$^{2+}$ + H$_2$O $\rightarrow$ (2H)Me$^+$ + MgO (Kohlstedt, 2006; Kohlstedt & Mackwell, 1998). A $C_{H2O}$ exponent larger than 1.0 also suggests that defect concentration and mobility are both enhanced by hydration (Fei et al., 2018a).

The H$_2$O dependence of $\sigma_{ionic[100]}$ is not determined in this study because it is masked by small polaron conduction at relatively low temperatures (<1700 K), whereas significant dehydration occurs at >1700 K. We assume that $\sigma_{ionic[100]}$ has the same $C_{H2O}$ dependence as other crystallographic orientations.
Table 3

| Axis  | r        | \( \log(e^{\text{ionic,0}[hkl]}) \) (K·S/m) | \( E_{\text{ionic}[hkl]} \) (kJ/mol) | \( V_{\text{ionic}[hkl]} \) (cm\(^3\)/mol) | \( \log(e^{\text{sp,0}[hkl]}) \) (S/m) | \( E_{\text{sp}[hkl]} \) (kJ/mol) | \( V_{\text{sp}[hkl]} \) (cm\(^3\)/mol) | Misfit |
|-------|----------|--------------------------------------------|----------------------------------|--------------------------------------------|--------------------------------|--------------------------------|--------------------------------|-------|
| [001] | 9.5 (4)  | 337 (15)                                   | 4.2 (4)                          | 1.5 (2)                                    | 117 (13)                     | 0.5 (7)                        | 0.04                           |       |
| [010] | 11.6 (4) | 396 (25)                                   | 3.2 (2)                          | 2.7 (2)                                    | 163 (25)                     | –0.2 (2)                       | 0.06                           |       |
| [001] | 11.8 (4) | 385 (15)                                   | 4.1 (4)                          | 2.7 (3)                                    | 139 (13)                     | 0.5 (7)                        | 0.15                           |       |
| Isotropic | 11.1     | 372                                         | 3.8                              | 2.3                                        | 139                         | 0.3                            | –                 |       |

*The \( \text{H}_2\text{O} \) content exponent, \( r \), is assumed to be the same for different orientations.

Theoretically, we cannot exclude the possibility of anisotropic \( C_{\text{H}_2\text{O}} \) dependence, but it is a reasonable assumption because H substitution is independent of orientation, whereas the weakening of \( \text{Mg}^{2+} \) bonding by hydration along different directions is expected to be similar because the overall bond strength of \( \text{Mg}^{2+} \) is weakened.

### 3.4. Ionic Conductivity of Olivine Under Asthenospheric Conditions

Using the pressure, temperature, \( C_{\text{H}_2\text{O}} \), and crystallographic dependences determined in this study, the integrated models of anisotropic conductivity along \([hkl]\) axis (\( \sigma_{\text{ionic}[hkl]} \) and \( \sigma_{\text{sp}[hkl]} \) for ionic and small polaron conductivities, respectively) and isotropic conductivity (\( \sigma_{\text{ionic}[\text{iso}]} \) and \( \sigma_{\text{sp}[\text{iso}]} \), respectively) in hydrous olivine under asthenospheric conditions are given as

\[
\sigma_{\text{ionic}[hkl]} = \sigma_{\text{ionic}[\text{anhydrous}][hkl]} + \sigma_{\text{ionic}[\text{hydrous}][hkl]} = \frac{e^{\sigma_{\text{ionic,0}[hkl]} T}}{C_{\text{H}_2\text{O}}} \exp \left( \frac{E_{\text{ionic}[hkl]} + PV_{\text{ionic}[hkl]}}{RT} \right) \quad (4)
\]

\[
\sigma_{\text{ionic}[\text{iso}]} = \left( \sigma_{\text{ionic}[100]} \times \sigma_{\text{ionic}[010]} \times \sigma_{\text{ionic}[001]} \right)^{1/3} \quad (5)
\]

\[
\sigma_{\text{sp}[hkl]} = \sigma_{\text{sp,0}[hkl]} \exp \left( \frac{E_{\text{sp}[hkl]} + PV_{\text{sp}[hkl]}}{RT} \right) \quad (6)
\]

\[
\sigma_{\text{sp}[\text{iso}]} = \left( \sigma_{\text{sp}[100]} \times \sigma_{\text{sp}[010]} \times \sigma_{\text{sp}[001]} \right)^{1/3} \quad (7)
\]

The bulk conductivity of anisotropic and isotropic models are

\[
\sigma_{\text{bulk}[hkl]} = \sigma_{\text{ionic}[hkl]} + \sigma_{\text{sp}[hkl]} \quad (8)
\]

\[
\sigma_{\text{bulk}[\text{iso}]} = \sigma_{\text{ionic}[\text{iso}]} + \sigma_{\text{sp}[\text{iso}]} \quad (9)
\]

The fitting parameters of \( \sigma_{\text{ionic,0}}, E_{\text{ionic}}, V_{\text{ionic}}, \sigma_{\text{sp,0}}, E_{\text{sp}}, \) and \( V_{\text{sp}} \) are listed in Table 3. The \( C_{\text{H}_2\text{O}} \) is in wt. ppm based on Withers et al. (2012), \( \sigma_{\text{ionic}[\text{anhydrous}][hkl]} \) is ionic conductivity in dry olivine, and \( \sigma_{\text{ionic}[\text{hydrous}][hkl]} \) is ionic conductivity owing to \( \text{H}_2\text{O} \) incorporation. Because \( \sigma_{\text{ionic}[\text{anhydrous}][hkl]} \) based on completely dry experiments at ambient pressure (Constable et al., 1992) is more than 1 order of magnitude lower than our experimental data with \(~20\) wt. ppm \( \text{H}_2\text{O} \) (Figure 8), the contribution of \( \sigma_{\text{ionic}[\text{anhydrous}][hkl]} \) is considered negligible in this study, as expressed in equation 4. The transition of ionic conduction from an anhydrous to hydrous mechanism should occur at \( C_{\text{H}_2\text{O}} \) much lower than \(~20\) wt. ppm. The \( r \) is assumed to be \( 1.3 \pm 0.2 \) for different crystallographic orientations and independent of temperature and pressure, whereas \( E_{\text{ionic}} \) and \( V_{\text{ionic}} \) are assumed to be independent from \( C_{\text{H}_2\text{O}} \) (Table 3). These assumptions are expected to have little effect on the simulated results because our conductivity data were obtained under asthenospheric \( P-T \) conditions, and the range of \( C_{\text{H}_2\text{O}} \) extrapolation is small owing to the relatively low (30–60 wt. ppm) \( \text{H}_2\text{O} \) content of olivine in the depleted MORB mantle (Demouchy & Bolfan-Casanova, 2016; Katsura et al., 2017).

The simulated results of \( \sigma_{\text{ionic}} \) for isotropic and anisotropic models under the topmost asthenospheric conditions (3 GPa) are plotted in Figures 9a and 9b, whereas the bulk conductivity, which is the summation of different mechanisms, are plotted in Figure 9c. The \( \sigma_{\text{ionic}} \) in this study shows a comparable
temperature dependence with the previously reported ionic conductivity data (e.g., Constable et al., 1992), indicating the same conduction mechanisms (Figures 9a and 9b). After adjusting to a \( C_{H_2O} \) of 1 wt. ppm, the isotropic \( \sigma_{ionic} \) from this study is comparable with \( \sigma_{ionic} \) reported in dry olivine at ambient pressure (Constable et al., 1992). However, by adding 60 wt. ppm \( H_2O \) (the maximum \( C_{H_2O} \) for olivine in the depleted mantle by considering \( H_2O \) partitioning in upper mantle minerals, Demouchy & Bolfan-Casanova, 2016), \( \sigma_{ionic} \) is enhanced by about 2 orders of magnitude (Figure 9a). We have \( \sigma_{ionic}[001] \gg \sigma_{ionic}[100] \approx \sigma_{ionic}[010] \) in olivine with 60 wt. ppm \( H_2O \), which has the same order of anisotropy and comparable temperature dependence as that under dry conditions at ambient pressure (Constable et al., 1992) although the absolute values differ by more than 1 order of magnitude due to the \( H_2O \) enhancement.

The isotropic \( \sigma_{ionic} \) from our model at 10 GPa is within experimental uncertainty consistent with that reported by Yoshino et al. (2009) under similar conditions due to the negative pressure dependence (Figure 9a). The 3 GPa data are comparable with that estimated from hydrogen diffusivity as well by assuming a linear relationship between \( C_{H_2O} \) and hydrogen-related \( \sigma \) (Du Frane & Tyburczy, 2012; Novella et al., 2017), which is not surprising because hydrogen diffusion is the migration of protons into/out of cation sites and is therefore also controlled by Mg defects.
Owing to the H$_2$O-enhancement of $\sigma_{\text{ionic}}$, the bulk conductivity obtained in this study with 60 wt. ppm H$_2$O is clearly higher than values reported under dry conditions (Constable, 2006; Constable et al., 1992; Xu et al., 1998) and comparable with that estimated from Mg diffusion by assuming an $C_{\text{H}_2\text{O}}$ exponent of 1.3 (Fei et al., 2018a) (Figure 9c). However, although the absolute values of our bulk conductivity data are identical to Gardés et al.’s (2014) model at 1600–1700 K, the temperature dependences are completely different, indicating the dominance of different mechanisms. This inconsistency is likely caused by an overestimation of proton conductivity in previous studies (see discussion in the supporting information).

The comparison of $\sigma_{\text{ionic}}$ and $\sigma_p$ (proton conduction) shows a mechanism transition from small polaron to ionic conduction at 1600–1650 K (Figures 9a and 9b). This transition temperature, although pressure- and C$_{\text{H}_2\text{O}}$ dependent, is much lower than the previously estimated values (>1750 K, Gardés et al., 2014; Yoshino et al., 2009) and comparable with the asthenospheric geotherm (Katsura et al., 2017; Turcotte & Schubert, 2002). Therefore, by H$_2$O-enhancement, $\sigma_{\text{ionic}}$ of olivine is nonnegligible under asthenospheric conditions. It may contribute significantly, or dominate the bulk conductivity of olivine in the asthenosphere especially in the shallow region beneath young plates where the pressure is relatively low and temperature is relatively high.

Based on our model, the bulk conductivity of olivine with 60 wt. ppm H$_2$O is $>10^{-2}$ S/m when the temperature is above 1600 K (Figure 9c), which is comparable with the high conductivity observed at the topmost asthenosphere beneath young plates (Baba et al., 2006). On the other hand, the asthenosphere is associated with low seismic velocity, which cannot be attributed to olivine hydrated with only tens of wt. ppm H$_2$O (Cline et al., 2018). By considering the fact that the high conductivity is observed mostly beneath young plates (summarized in Katsura et al., 2017) whereas the low seismic velocity zone is detected nearby globally, the origins of these geophysical features could be different, although they occur at similar depths.

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