Electrical conductivity of wadsleyite at high temperatures and high pressures

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\textbf{A B S T R A C T}

The electrical conductivity of wadsleyite aggregates has been determined under the broad range of thermodynamic conditions using the impedance spectroscopy for a frequency range of \(10^{-2}\) to \(10^6\) Hz. Two branches are observed in the complex impedance, one (at high frequency range) showing a half circle originated at \(Z\) (real part of impedance) = \(Z^r\) (imaginary part of impedance) = 0 in the \(Z^r-Z^i\) plot, and another branch in the low frequency range. The results from high frequency semi-circles correspond to the electric properties of a sample, whereas the results from a low frequency branch correspond to the electrode effects. From the analysis of the results from the semi-circles, we have identified two distinct mechanisms of electrical conduction having different activation enthalpies and different sensitivity to oxygen fugacity and water content. One mechanism dominating at water-poor condition has a high activation enthalpy (~147 kJ/mol) and the conductivity increases with oxygen fugacity. We suggest that electrical conduction in this regime is due to charge transfer involving ferric iron (“polaron” conduction). Under water-rich conditions, electrical conductivity increases with water content but decreases with oxygen fugacity, and the activation enthalpy is smaller (~88 kJ/mol). We infer that electrical conduction in this regime is due to protons. The activation enthalpy in this regime is insensitive to water content and the conductivity is proportional to water content, \(C_w\), as \(\sigma \propto C_w^r\) with \(r\sim 0.72\). The value of \(r\) is smaller than one suggests that minority defects such as \(H_d\) or \(H^+\) are responsible for electrical conduction. Our results show that a completely dry transition zone is incompatible with most of the geophysical observations on the mantle transition zone, and some water (~0.1–0.3 wt.% in the Pacific) is required to explain the observed electrical conductivity.

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1. Introduction

Electrical conductivity of minerals may be enhanced by the dissolution of water (hydrogen) (Karato, 1990). If this hypothesis is true, then we can in principle infer the water content in Earth’s interior by comparing geophysically inferred conductivity profiles with laboratory data on the relation between electrical conductivity and water content (Karato, 2006). A few experimental studies have been conducted to test this hypothesis (wadsleyite: (Huang et al., 2005; Yoshino et al., 2008a; Romano et al., 2009)), olivine: (Wang et al., 2006; Yoshino et al., 2006)). However, there are complications in the experimental measurements of electrical conductivity and there have been some discrepancies among different studies on this topic. (Huang et al., 2005) found a large influence of water on the electrical conductivity of wadsleyite and estimated the water content in the transition zone is ~0.1–0.2 wt.%. In contrast, Yoshino et al. (2008a) and Manthilake et al. (2009) presented results somewhat different from those by Huang et al. (2005) and argued that the transition zone (in the Pacific) is “dry” (water-free). Yoshino et al. (2008a) and Manthilake et al. (2009) determined the electrical conductivity of wadsleyite under broader temperature and water content conditions than Huang et al. (2005) but using a different experimental method. Karato and Dai (2009) provided some discussions on the influence of different methods of conductivity measurements (see also (Yoshino and Katsura, 2009)). Also, the influence of another important parameter, namely oxygen fugacity was not determined in these previous studies.

Therefore the main purpose of this study is to revisit the issue of influence of water on the electrical conductivity of wadsleyite through a more extensive study than (Huang et al., 2005) to establish the relationship between physico-chemical variables and electrical conductivity on the more solid basis and to explore the causes for differences in the results from two research groups. We have expanded our previous study (Huang et al., 2005) in three respects: (i) we now add the results of conductivity measurements for a nearly water-free sample, (ii) the complex impedance was measured to lower frequencies (to 0.01 Hz) to investigate the causes for the discrepancy between the two sets of results, (iii) the influence of oxygen fugacity was determined to provide a firmer constraint on the mechanisms of electrical conductivity and (iv) the temperature and water content sensitivities were determined under a broader range of conditions.

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2. Experimental procedures

2.1. Sample preparation

Wadsleyite samples were synthesized from San Carlos olivine by phase transformation at 16 GPa and 1573 K. About 1.5 wt.% of orthopyroxene was added to buffer the oxide activity. Powder samples of olivine and orthopyroxene mixture were put into a metal capsule (Mo, Ni and Re were used to test the influence of different oxygen fugacity). Both synthesis and conductivity measurements were made using the same oxygen fugacity buffer. Our previous experience showed that under these conditions, the oxidation conditions of samples are well buffered by the metal and metal oxide reactions (e.g., (Nishihara et al., 2006, 2008)) and the presence of metal oxide such as ReO₂ was confirmed in most cases although the detection of metal oxide was difficult in cases where the volume of metal oxide is small. Each synthetic sample was examined by the micro-Raman spectroscopy to ensure that they are indeed wadsleyite. We obtained dense polycrystalline wadsleyite (with a small amount of majorite garnet) with a range of water content.

Water content of the samples was controlled in two different ways. In some synthesis runs, no water was added to a sample capsule, but some water was dissolved in the samples presumably from adsorbed water in the cell assembly. In other cases where a larger amount of water is to be dissolved, we add a talc–brucite mixture as described by Huang et al. (2005). The synthesis of a truly “dry” wadsleyite sample is not straightforward as discussed by Huang et al. (2005) and Nishihara et al. (2006). We used carefully dried parts and starting powder sample was inserted in an Au–Pd capsule with another metal foil to control the oxygen fugacity. As we will show, even the best case we had so far, a sample still had some water (less than 8 ppm H/Si), but that was the driest sample of wadsleyite that we ever had.

2.2. Sample characterization

Both before and after each electrical conductivity measurement, the grain-size was measured by an intercept method using a scanning electron microscope. The grain-size is nearly homogeneous in all samples within an error of measurements (~20%). There was no detectable change in grain-size during conductivity measurements. However, the influence of grain-size on electrical conductivity was not investigated systematically in this study. Similarly the previous studies on olivine aggregates by Huang et al. (2005) and Roberts and Tyburczy (1991) did not find a large effect of grain-size. Therefore, we consider that we may ignore the grain-size effect here.

Fourier-transformed infrared (FT-IR) spectroscopy was used to determine the water content. For all samples, FT-IR measurements were made both before and after each conductivity measurements for the wave-number range of 1000 to 4000 cm⁻¹. FT-IR absorption spectra of most of the samples are shown in Fig. 1. The doubly polished samples with a thickness of less than 60 μm were prepared for the FT-IR analysis. The FT-IR absorption spectra of samples were taken using an un-polarized IR beam with a mid-IR light source, a KI beam splitter and an MCT detector. One hundred twenty eight times were accumulated for each spectrum. Apertures of 100×100 μm were used to ensure a large effect of grain-size during conductivity measurements. Consequently, the water content estimate for wadsleyite has relatively small errors, on the order of ~10%. However, when the total water content becomes small, the relative errors become larger. For example, for the driest sample, our measurement showed ~8 ppm H/Si, but this is close to the detectability limit and errors are as large as ±50% in this case. We also note that the peak frequency of absorption for this sample is different from the peak frequencies of other water-rich samples indicating a different hydrogen-related species is involved in this sample (see (Nishihara et al., 2008)). Therefore the results from this sample cannot be compared with the results from other water-rich samples directly.

As we will show later, a sample with the smallest water content showed different behavior in electrical conductivity than samples with higher water content. We will call that sample “dry” wadsleyite and others as “wet” wadsleyite. Water content was determined both before and after the electrical conductivity measurements of hydrous sample, and the water loss is not more than 10%.

2.3. Conductivity measurements

The experimental sample assembly is shown in Fig. 2. Pressure was generated by a 1000-ton Kawai-type hydraulic press using eight cubic tungsten carbide anvils (Spec: 26 × 26 × 26 mm³) with an 8 mm truncated carbide edge length. Pressure calibrations were made using the phase transitions of coesite and stishovite (Zhang et al., 1996), 9.5 GPa and 1573 K), as well as forsterite and wadsleyite (Morishima et al., 2004), 14.5 GPa and 1573 K). A Cr₂O₃-doped (5%) semi-sintered octahedral MgO was used as a pressure medium. In order to avoid the influence of adsorbed water on the measurement of electrical conductivity, MgO was dried at 1273 K in air prior to sample assembly. In order to control the oxygen fugacity of the sample

\[
C_W = \frac{B_i}{150ε} \int K(v) \frac{dv}{(3780 - v)}
\]

where \(C_W\) is the molar concentration of hydroxyl (H/10⁶ Si), \(B_i\) is the density coefficient (4.08 × 10⁻⁸ cm H/10⁶ Si), \(ε\) is the orientation factor (1/3), and \(K(v)\) is the absorption coefficient in cm⁻¹ at the wave-number \(v\) (cm⁻¹).
chamber and reduce the leakage currents, a corresponding metal foil shielding was placed between a sample and an MgO insulation tube. A disk-shaped sample (Ø1.6×0.4 mm) was placed between two electrodes that were surrounded by alumina rings. The metal of electrode and the shielding foil are made of the same material as the capsule used for the synthesis of the sample. The temperature was measured by a W5%Re–W26%Re thermocouple that was placed on the surface of sample and used as one of the electrodes (a thermocouple is connected to an electrode but does not directly touch the sample and therefore a thermocouple will not directly affect the oxygen fugacity of a sample). The relative experimental errors of the temperature and pressure gradient were estimated to be ~10 K and ~0.5 GPa, respectively.

The pressure was first raised at the rate of ~2.5 GPa/h to a designated value. After the pressure is set to the desired value, temperature was raised at the rate of ~100 K/min to the preset value and the impedance spectroscopy measurements were made at various temperatures. After the temperature reached to an each value, the ZView program of a Solartron-1260 Impedance/Gain-Phase analyzer was run to determine the complex impedance for the frequency range of \( f = 10^{-2} \text{–} 10^{6} \text{Hz} \). The impedance semi-circle arc of high frequency branch (from \( 10^{6} \text{Hz} \) to \( 10^{2} \text{–} 10^{3} \text{Hz} \)) was fitted by virtue of an equivalent circuit of the ZView program that was made up of a resistance connected in parallel with a capacitor. From the fitting of the semi-circle to this model, we determine the conductivity of a sample.

The frequency range used in this study is broader than that used by Huang et al. (2005). This “impedance spectroscopy” approach is critical when there is a mechanism of charge built-up. When electric charge is built-up somewhere in the sample (or at the electrode), electric response of a sample to applied voltage includes capacitance as well as resistance. In order to make correction for the capacitance effect, it is necessary to analyze the data from a broad frequency range. However, in some studies (e.g., (Katsura et al., 1998; Yoshino and Katsura, 2009b)), they range. However, in some studies (e.g., (Katsura et al., 1998; Yoshino et al., 2008b; Yoshino and Katsura, 2009b)), they range. However, in some studies (e.g., (Katsura et al., 1998; Yoshino et al., 2008b; Yoshino and Katsura, 2009b)), they range.

The presence of two branches in the impedance spectroscopy implies the presence of two processes of charge transfer and/or blocking. The first semi-circle starting from the origin (\( Z' = Z'' = 0 \)) corresponds to a parallel combination of a resistor and a capacitor, and the second branch (“tail”) at low frequencies corresponds to some blocking effects of electric current either at electrodes or at grain-boundaries (or both) (Macdonald et al., 1982; Cemgil, 1996). Therefore we determined the conductivity from the fitting of the first semi-circle to equivalent circuit that is made of a parallel combination of resistor and capacitor.

Fig. 4 shows the results for the resistance measurements for a temperature cycling. We found no large hysteresis suggesting that the conductivity that we measure represents nearly equilibrium value for a given physical and chemical conditions at each measurement. This is also consistent with the observation that no appreciable water loss is detected in our study.

In order to make sure that the results are not affected by the leak current through the sample and the shield separated by an \( \text{Al}_2\text{O}_3 \) ring, we measured the “background resistivity”. In this background test, a sample is replaced with an \( \text{Al}_2\text{O}_3 \) disc with the dimension of...
The results are shown in Fig. 7. The electrical conductivity increases with temperature. The relationship between electrical conductivity and temperature approximately follows the Arrhenius relation, \( \sigma \propto \exp \left( \frac{-H^*}{RT} \right) \), where \( H^* \) is the activation enthalpy. However, the activation enthalpy is different between “dry” and water-rich samples: \( H^* = 147 \pm 3 \text{ KJ/mol} \) for a dry sample whereas \( H^* = 88 \pm 10 \text{ KJ/mol} \) for water-rich samples. It should be noted that we also determined activation enthalpies for “wet” samples with different water content individually. The results are shown in Table 2. However, we observed that the activation enthalpy in “wet” samples is nearly independent of water content. A sample with an intermediate value of water content (K865) shows a mixed trend: at low temperatures, the slope in this plot follows that of water-rich samples, but the slope becomes close to that of a dry sample at higher temperatures. This suggests that there are two independent mechanisms of electrical conduction in these samples. Note that the activation enthalpy for water-rich sample does not depend on the water content in the water content range explored in our study.

Fig. 6 shows the relation between water content and electrical conductivity in water-rich samples (for the Mo–MoO\(_2\) buffer). The electrical conductivity increases with water content following \( \sigma \propto C^*_W \) with \( r = 0.72 \pm 0.08 \) that is consistent with the results by Huang et al. (2005) and is similar to the results for olivine (Wang et al., 2006) and pyrope garnet (Dai and Karato, 2009).

In order to obtain additional constraints on the mechanisms of electrical conductivity in two regimes (“dry” and “wet” (“water-rich”) regimes), we have determined the influence of oxygen fugacity on electrical conductivity using three different oxygen fugacity buffers. The results are shown in Fig. 7. The electrical conductivity increases with increasing oxygen fugacity for a “dry” sample, whereas the electrical conductivity decreases with oxygen fugacity for water-rich samples. If we use the relation \( \sigma \propto f^{1/2}_\text{fl} \), \( q = 0.050 \pm 0.009 \) for “dry” sample and \( q = -0.058 \pm 0.004 \) for “wet” sample.

The differences in activation enthalpy and in the dependence on oxygen fugacity for two types of samples (“dry” and “wet” (“water-rich”)) clearly indicate that the mechanism of electrical conductivity is different under these two conditions. Consequently, we use the following formula to analyze the data,

\[
\sigma = \sigma_1 + \sigma_2
\]

where \( \sigma_1 \) is the electrical conductivity of a “dry” sample and \( \sigma_2 \) is the electrical conductivity of “wet” (water-rich) samples. For each mechanism, we use the following formula,

\[
\sigma = A \cdot C^*_W \cdot f^{\alpha}_{\text{fl}} \cdot \exp \left( \frac{-Q^*}{RT} \right)
\]

where \( A, r, q \) are the constants, \( C^*_W \) is the water content, \( H^* \) is the activation enthalpy, \( R \) is the gas constant and \( T \) is temperature. The parameters for each mechanism are summarized in Table 2. The fitted parameter values for the electrical conductivity of “wet” and “dry” wadsleyite are listed in Table 2.

### Table 1

<table>
<thead>
<tr>
<th>Run no.</th>
<th>P (GPa)</th>
<th>T (K)</th>
<th>Water content (H/10^6 Si)</th>
<th>Oxygen buffer</th>
<th>Grain size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Before experiment</td>
<td>After experiment</td>
<td></td>
</tr>
<tr>
<td>K736</td>
<td>15</td>
<td>873–1273</td>
<td>1400</td>
<td>1280</td>
<td>Mo–MoO(_2)</td>
</tr>
<tr>
<td>K743</td>
<td>15</td>
<td>873–1273</td>
<td>34,000</td>
<td>32,000</td>
<td>Mo–MoO(_2)</td>
</tr>
<tr>
<td>K757</td>
<td>15</td>
<td>873–1673</td>
<td>&lt;8</td>
<td>&lt;9</td>
<td>Mo–MoO(_2)</td>
</tr>
<tr>
<td>K792</td>
<td>15</td>
<td>873–1273</td>
<td>13,000</td>
<td>12,000</td>
<td>Mo–MoO(_2)</td>
</tr>
<tr>
<td>K814</td>
<td>15</td>
<td>873–1273</td>
<td>12,000</td>
<td>11,000</td>
<td>Ni–NiO</td>
</tr>
<tr>
<td>K819</td>
<td>15</td>
<td>873–1273</td>
<td>&lt;5</td>
<td>&lt;7</td>
<td>Re–ReO(_2)</td>
</tr>
<tr>
<td>K820</td>
<td>15</td>
<td>873–1273</td>
<td>&lt;7</td>
<td>&lt;8</td>
<td>Re–ReO(_2)</td>
</tr>
<tr>
<td>K865</td>
<td>15</td>
<td>873–1473</td>
<td>360</td>
<td>350</td>
<td>Mo–MoO(_2)</td>
</tr>
</tbody>
</table>

### Table 2

Parameter values for the electrical conductivity of wadsleyite.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Log(\sigma) (A(S/m))</th>
<th>r</th>
<th>(H^*) (KJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet</td>
<td>2.5 ± 0.5</td>
<td>0.72 ± 0.08</td>
<td>88 ± 10</td>
</tr>
<tr>
<td>0.22 wt.%</td>
<td>2.5 ± 0.2</td>
<td>0.72</td>
<td>88 ± 3</td>
</tr>
<tr>
<td>0.082 wt.%</td>
<td>2.4 ± 0.1</td>
<td>0.72</td>
<td>87 ± 3</td>
</tr>
<tr>
<td>0.009 wt.%</td>
<td>2.5 ± 0.2</td>
<td>0.72</td>
<td>86 ± 3</td>
</tr>
<tr>
<td>0.0023 wt.%</td>
<td>2.6 ± 0.3</td>
<td>0.72</td>
<td>91 ± 6</td>
</tr>
<tr>
<td>Dry</td>
<td>2.1 ± 0.1</td>
<td>0.72</td>
<td>147 ± 3</td>
</tr>
</tbody>
</table>

The relation \( \sigma = A \cdot C^*_W \cdot f^{\alpha}_{\text{fl}} \cdot \exp \left( \frac{-Q^*}{RT} \right) \) is used. For individual fitting for each water content, the corresponding value of \( C^*_W \) (with \( r = 0.72 \)) was used (the assumed value of \( r \) does not influence the estimated \( H^* \) and therefore the error in \( r \) is not included in the estimate of \( A \) and \( H^* \) for individual fitting). The reported errors are the one standard deviation, and include the propagation of errors in individual measurements (errors in water content, temperature and electrical conductivity). The errors and the value of \( H^* \) for 0.0023 wt.% sample are larger than those of other “wet” samples due to the appreciable contributions of two mechanisms of conduction under these conditions leading to a curvature in the log(conductivity) versus 1/T (temperature) plot (see Fig. 5). Conductivity is assumed to be independent of grain-size (as shown by Huang et al., 2005).
The observed different activation enthalpy and different dependence on oxygen fugacity for “dry” and “wet” (water-rich) samples are strong evidence for the operation of different mechanisms of electrical conduction in these two types of samples. In particular, the dependence of conductivity on oxygen fugacity and water fugacity (the exponent $r$ and $q$ in Eq. (31)) provide strong constraints on the nature of point defects involved in electrical conductivity (see Chapter 10 of Karato (2008) for details). The observed positive exponent for oxygen fugacity for a “dry” sample is consistent with the charge transfer by ferric iron (Fe) with charge neutrality condition either $\left[ Fe^{3+} \right] = 2\left[ V_{an}^{\prime} \right]$ (this model predicts $r = 1/2$ and $q = -1/12$) or $H^+$ with the charge neutrality condition of $\left[ Fe^{3+} \right] = [H^+]$ ($r = 3/4$ and $q = -1/8$) is a plausible model (Karato, 2008). The presence of such minority defects in wadsleyite is documented by Nishihara et al. (2008). This means that the minority defects such as $H^+$ or $H_2O$ has higher mobility than the majority defect, $2H\_2O$. Again, however, the absolute value of $q$ ($= -0.058$) is less than these model predictions, suggesting that the experimental conditions may span more than one charge neutrality conditions or chemical equilibrium was only partial.

4.2. A comparison to previous studies

The present results are in good agreement with those by Huang et al. (2005), although the parameter range explored is much broader in the present study than that in Huang et al. (2005). For example, we have determined the temperature dependence of conductivity under a broader range of conditions, and new results on the influence of oxygen fugacity were obtained.

However, our results are not consistent with those by Yoshino et al. (2008a) and Manthilake et al. (2009). As discussed in detail by Karato and Dai (2009), most of the differences between our results and those by Yoshino et al. (2008a) and Manthilake et al. (2009) are due to the difference in the method of conductivity measurements (see also Romano et al. (2009)) and the difference in water content in “dry” samples. Essentially, the use of one (or two) low frequency to determine electrical conductivity results in a systematic bias for the determined conductivity due to the influence of charge blocking at electrodes. This influence is greater for samples with higher water content. This point is shown in Fig. 8. It is seen that the difference in results from one low frequency measurements and impedance spectroscopy is larger for samples with larger water content. Also, the difference is larger at higher temperatures (under high water content conditions). We can largely reproduce Yoshino et al.’s results (Yoshino et al., 2008a) from our data if we use one frequency (0.01 Hz). Consequently, we consider that the most of the differences are due to the differences in the method of conductivity measurements.

The above analysis also implies that the reported water content dependence of activation enthalpy by Yoshino et al. (2008a) may be an experimental artifact. Both in Huang et al. (2005) and this study, we show that the activation enthalpy under water-rich conditions is insensitive to water content. As we discussed in detail before (see also (Karato and Dai, 2009)), one fundamental problem of Yoshino et al.’s (2008a) approach is the use of a single low frequency to determine the conductivity that gives rise to a systematic bias on the inferred conductivity. This difference becomes larger at higher water content and higher temperature (in the water-rich regime), and consequently will result in the biased estimates of activation enthalpy. To evaluate the magnitude of this effect, we have calculated the activation enthalpy using our method as well as Yoshino et al.’s. (2008a) method. The results are compared in Fig. 9. It is seen that when we use Yoshino...
et al.’s method, we reproduce water content-dependent activation enthalpy that they reported, but the activation enthalpy is insensitive to water content, if the impedance spectroscopy technique is used. It is also noted that a sample with a small water content (K865) shows the influence of both protons (at low temperatures) and polarons (at high temperatures). The composite conductivity equation with parameters shown in Table 2 reproduce our results as shown in Fig. 5. Yoshino and Katsura (2009a) claimed that our data are internally inconsistent because the results from low water content samples (K865 and K787) are not compatible with other data with higher water contents. The above analysis shows that their claim is invalid because of their incorrect interpretation of results FT-IR study of water content and speciation.

We also note that Yoshino et al. (2008a) and Manthilake et al. (2009) measured electrical conductivity of “wet” samples at lower temperatures than most of our measurements. Consequently, conductivity mechanisms operating under their experimental conditions might be different from those in our “wet” samples and this is a possible additional factor that may cause the difference in the results. In any case, either due to the artifact cause by the use of inappropriate method or by the use of the low temperatures (for “wet” samples), we conclude that the results by Yoshino et al. (2008a) and Manthilake et al. (2009) on “wet” wadsleyite cannot be applied to Earth’s interior.

4.3. Geophysical implications

The present study has provided additional data on the electrical conductivity of wadsleyite for a broad range of thermo-chemical conditions that forms a basis for estimating water content in the transition zone. Given a much lower solubility of hydrogen in garnet (Katayama et al., 2003) than that in wadsleyite (Kohlstedt et al., 1996), we may model the upper transition zone (410–520 km) as a mixture of highly conductive wadsleyite and less conductive majorite garnet. Because the more conductive component, wadsleyite, is volumetrically dominant, we can assume that wadsleyite forms a connected network. In such a case, geophysical estimates from a model corresponding to the upper bound (e.g., (McLachlan et al., 1990)) in the upper portion of the transition zone ranging from \( \sigma = \sigma_{wad}(T, C_w) \) with \( \beta \approx 0.6 \) to \( \sigma_{wad}(T, C_w) = \sigma_1(T) + \sigma_2(T, C_w) \) that is given by the present results (we assumed 60% of wadsleyite and 40% of majorite).

Fig. 10 shows the \( T \)–water content \( C_w \) relationship corresponding to various conductivity values. The oxygen fugacity corresponding to Mo–MoO\(_2\) buffer is assumed. A grey thick curve shows a boundary between proton-dominated regime and polaron-dominated regime. Most of conductivity data for Earth’s transition zone fall into the proton-dominated regime.
robust estimates of water content, one needs to obtain better experimental data electrical conductivity of majorite garnet and independent estimates of temperature.

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