**Some notes on hydrogen-related point defects and their role in
the isotope exchange and electrical conductivity in olivine**

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Abstract

Nominally anhydrous minerals such as olivine dissolve hydrogen in a variety of forms including free (or interstitial) proton (H°) and two protons trapped at the M-site ($(2H)_M^\times$). The strength of chemical bonding between protons and the surrounding atoms are different among different species, and consequently protons belonging to different species likely have different mobility (diffusion coefficients). I discuss the role of diffusion of protons in different species in the isotope exchange and hydrogen-assisted electrical conductivity adding a few notes to the previous work by Karato (2013) including a new way to test the model. I conclude that in the case of isotope exchange, the interaction among these species is strong because diffusion is heterogeneous, whereas there is no strong interaction among different species in electrical conduction where diffusion is homogeneous (in an infinite crystal). Consequently, the slowest diffusing species controls the rate of isotope exchange, whereas the fastest diffusing species controls electrical conductivity leading to a different temperature dependence of activation energy and anisotropy.

This model explains the differences in the activation energy and anisotropy between isotope diffusion and electrical conductivity, and predicts that the mechanism of electrical conductivity changes with temperature providing an explanation for most of the discrepancies among different experimental observations at different temperatures except for those by Poe et al. (2010) who reported anomalously high water content dependence and highly anisotropic activation energy. When the results obtained at high temperatures are used, most of the geophysically observed high and highly anisotropic electrical conductivity in the asthenosphere can be explained without invoking partial melting.

Introduction

Since the first suggestion by Karato (1990) of the enhancement of electrical conductivity by hydrogen in olivine, a number of experimental studies have been conducted on the role of hydrogen in electrical conductivity in olivine and other minerals. The importance of hydrogen in electrical conductivity is now well established for most minerals (e.g., (Karato and Wang, 2013; Yoshino and Katsura, 2013)). However, there are some discrepancies among the published experimental results and the degree to which hydrogen-enhanced conductivity explains the geophysical observations is still controversial (see above reviews). This is partly caused by the subtleties in the experimental studies on electrical conductivity of materials containing hydrogen as impurities (i.e., impedance spectroscopy versus one-frequency measurement, the evaluation of hydrogen loss/gain during the measurements; see (Karato and Dai, 2009) and (Karato and Wang, 2013) for discussions of particular experimental studies), but also due to the complications in the manner in which hydrogen-related defects are incorporated and migrate in a mineral.

In this note, I will focus on the latter, i.e., the theoretical aspect and provide some additional discussions on the nature of hydrogen-related defects and their migration in olivine. Karato (2013) proposed a theoretical model of hydrogen-deuterium isotope exchange by diffusion in order to explain two major puzzles: (i) the discrepancies between diffusion and conductivity (largely different activation energy and anisotropy) and (ii) the discrepancies among different experimental studies conducted at different temperatures. The predictions of this model were tested by Dai and Karato (2014) where they showed that the mechanisms of electrical conduction change with temperature, and

at high temperatures, average conductivity is higher than those extrapolated from the previous low temperature results and anisotropy is substantially higher than that at lower temperatures. These results provide an explanation for the discrepancy among different experimental studies and imply that a majority of geophysical observations of electrical conductivity of the asthenosphere can be explained by the presence of geochemically reasonable amounts of hydrogen if the results at high-temperature are used. However, the model proposed by Karato (2013) involves subtle physics of point defects that is not familiar to a majority of mineral physicists and geophysicists. My discussions with fellow scientists motivated me to write this note to provide a more detailed explanation of the model and its implications.

Diffusion-conductivity discrepancies

The hypothesis of hydrogen-assisted conductivity was proposed based on the Nernst-Einstein relationship, viz.,

$$\sigma = f \frac{D c q^2}{RT} \quad (1)$$

where σ is electrical conductivity, f is the formation factor (a non-dimensional factor ~ 1), D is the diffusion coefficient of charge carrying species, c is the concentration of that species, q is the electric charge of that species, R is the gas constant and T is temperature. The Nernst-Einstein relationship implies that, for fixed water content, the activation energy and the anisotropy must be approximately the same for both hydrogen diffusion and hydrogen-assisted electrical conductivity.

However, a number of experimental studies on hydrogen-assisted electrical conductivity and hydrogen diffusion showed that the activation energy for hydrogen diffusion in olivine and wadsleyite (120-140 kJ/mol) are substantially higher than that of hydrogen-assisted electrical conductivity at relatively low temperatures (70-90 kJ/mol) (e.g., olivine: (Du Frane and Tyburczy, 2012; Kohlstedt and Mackwell, 1998; Wang et al., 2006), wadsleyite: (Dai and Karato, 2009; Hae et al., 2006; Huang et al., 2005)). In addition, although anisotropy in hydrogen diffusion in olivine single crystals is very large (a factor of 10-100; (Du Frane and Tyburczy, 2012; Kohlstedt and Mackwell, 1998)), hydrogen-assisted electrical conductivity in olivine measured at relatively low temperatures is nearly isotropic (Yang, 2012) (Poe et al. (2010) reported the results showing some anisotropy but the degree of anisotropy determined under their experimental conditions is much smaller than the degree of anisotropy of hydrogen diffusion: see a note on their work in the later part of this paper). Although the uncertainties in the measurements of diffusion coefficients are large, these discrepancies are so large that I believe that it is important to explain the cause of these discrepancies.

Extension of model of isotope exchange

The main purpose of my paper (Karato, 2013) was to solve this puzzle by extending the theory of isotope exchange to a case where multiple species are involved. The key concepts in my theory are (i) there are multiple H (hydrogen)- (and D (deuterium)-) bearing point defects in minerals such as olivine, (ii) different H- (or D-) bearing species have different diffusion coefficients (different mobility), and (iii) the concentration ratio of these defects maintains the local equilibrium defined by the free

energy of these species $\frac{C_i}{C_j} = \exp\left(-\frac{\Delta G_i - \Delta G_j}{RT}\right)$ (C_i : concentration of the i-th species, ΔG_i : free energy of the i-the species relative to the ground state (perfect crystal); **Fig. 1**).

The first point was clearly demonstrated in wadsleyite by Nishihara et al. (2008) based on infrared spectroscopy studies of samples prepared at a range of chemical conditions, but the presence of multiple hydrogen-bearing defects was also suggested in olivine from the experimental data of electrical conductivity (Karato, 2006; Wang et al., 2006) (see also a review by Karato and Wang (2013)). A free proton H° (could be considered as an interstitial proton, H_i°) and two protons at M-site vacancy $(2H)_M^\times$ likely have different diffusion coefficients because protons in $(2H)_M^\times$ are strongly trapped at the crystallographic site (M-site) while free proton is not strongly bonded to any site (I use the Kröger-Vink notation for point defects; see caption of Fig. 1).

In case of isotope exchange, the driving force is $-\frac{\partial c_i}{\partial x}$, and consequently diffusion itself will modify the concentrations of each species as a function of position. To illustrate this point, let us consider isotope exchange between two crystals in a case where diffusion coefficient of different species has the following order:

$D_{H^\circ, D^\circ} > D_{H_M^\circ, D_M^\circ} > D_{(2H)_M^\times, (2D)_M^\times}$ (D^X : diffusion coefficient of X). In this case, the

concentration ratio of various species would be out of equilibrium, if these species diffused independently (**Fig. 2**). It can also be shown that the charge balance condition is not satisfied as far as the properties of H-bearing and D-bearing defects are not exactly identical (e.g., the diffusion coefficient depends on the mass of the diffusing species, (Glicksman, 2000; Shewmon, 1989)). This would lead to the excess free energy of a specimen, and the various species will interact to minimize the excess free energy.

In contrast, the driving force for electrical conductivity is $-\frac{\partial\phi}{\partial x}$ (ϕ : electric potential) and is homogeneous (independent of the position) in an infinite crystal if a constant voltage is applied. Consequently, even though each species moves with different velocities, their motion is homogeneous, and the concentration of each species does not change during electrical conduction. Therefore there is no interaction among diffusing species in this case as far as we consider a case of infinite crystal (there is an important effect of electrode to introduce heterogeneous electric field. However, in an experiment, one uses electric field with a broad range of frequencies (impedance spectroscopy) to make a correction for this effect and determines the conductivity in an infinite crystal (Karato and Wang, 2013)).

Diffusion of multiple species involving some interactions (a case of isotope exchange) can be treated by assigning diffusion coefficient to each species and introducing the interaction term(s) with some constraints (charge balance, local equilibrium etc.). Such an approach is common in the theory of diffusion creep (Stocker and Ashby, 1973) and chemical reactions (Glicksman, 2000; Schmalzried, 1995) involving multiple species. I followed a similar approach to develop a theoretical model of the effective diffusion coefficient for isotopic exchange to obtain,

$$\tilde{D}_{isotope} = \frac{L}{\sum_i \frac{\alpha_i}{D_i}} \quad (2)$$

where D_i is the diffusion coefficient of the i-th species, α_i is the stoichiometric coefficient of the i-th species (Karato, 2013). Since there is no interaction among

diffusing species in case of electrical conductivity, electrical conductivity of a material with multiple species is given by the simple extension of the relation (1), viz.,

$$\sigma = \frac{1}{RT} \sum_i f_i D_i c_i q_i^2 \quad (3)$$

where f_i is the formation factor for the i-th species, c_i is the molar concentration of the i-th species, and q_i is the electric charge of the i-th species.

This model implies that for isotope exchange, the defect with the slowest diffusion coefficient controls the rate, while the defect with the highest diffusion coefficient (with non-negligible concentration) controls electrical conductivity. With the assumption that the activation energy for diffusion of $(2H)_M^\times$ is higher than that of H° (or H'_M), we expect that $(2H)_M^\times$ is the slow(est) diffusion species and H° (or H'_M) is the fast(est) diffusing species at relatively low temperatures. Therefore, under these conditions, the isotope exchange is likely controlled by the diffusion of $(2H)_M^\times$, while electrical conductivity is controlled by H° (or H'_M). Since protons in $(2H)_M^\times$ are strongly bonded to the surrounding atoms in a crystal, its diffusion is likely anisotropic. At low temperatures, diffusion of H° is faster than that of $(2H)_M^\times$, and hence H° will control electrical conductivity. In contrast to $(2H)_M^\times$, H° is weakly bonded and hence nearly isotropic. However, at high temperatures, diffusion of $(2H)_M^\times$ would become faster than H° because the activation energy for $(2H)_M^\times$ is larger than that for H° , and conductivity will be highly anisotropic. These are exactly what have been observed in the

experimental studies on isotope diffusion and electrical conductivity (Dai and Karato, 2014; Du Frane and Tyburczy, 2012; Kohlstedt and Mackwell, 1998; Yang, 2012).

In contrast, hydrogen-deuterium isotope exchange is controlled by diffusion of $(2H)_M^x$ at low temperatures, but by H° at high temperatures according to this theory. Consequently, when isotopic diffusion coefficients were measured under a broad range of temperatures, the activation energy at high temperature should be smaller than that at low temperatures and anisotropy is strong only at relatively low temperatures (**Fig. 3**). This is opposite to electrical conductivity where the activation energy should be higher and anisotropy is stronger than those at low temperatures. Experimental studies on isotope exchange under a broad range of temperature would provide a critical test although such a study is difficult because of the large uncertainties in the experimental determination of diffusion coefficients.

Discussion

A comparison to experimental results on electrical conductivity

Because the activation energies for diffusion are different among different species, the relative values of diffusion coefficients of various species will change with temperature. Therefore, at high temperature, the dominant species for electrical conductivity will be $(2H)_M^x$ and anisotropy will be higher than those at low temperatures ((Dai and Karato, 2014); **Fig. 3**). Consequently there should be a systematic difference in the apparent activation energy between low temperature and high temperature results. For instance, Wang et al. (2006) used a temperature range (873-1273 K) that is higher than the temperature range used by (Yoshino et al., 2006) (673-973 K) that partly explains the

difference between these studies particularly when extrapolated to higher temperatures (another reason for the difference between these studies is the use of different methods: impedance spectroscopy in Wang et al. (2006), and one low-frequency measurements in Yoshino et al. (2006) that causes systematic errors in the latter as demonstrated by Karato and Dai (2009)). The change in conduction mechanism as temperature increases was clearly shown by Dai and Karato (2014), but a similar trend can also be seen at high temperatures in the study by Yang (2012) on olivine single crystals (573-973 K).

However, the results by Poe et al. (2010) on hydrous single crystal olivine (at 773-973 K) are remarkably different from all other studies. Their results show largely different activation energies for different orientations (61 kJ/mol for [100], 88 kJ/mol for [010], 43 kJ/mol for [001])) and the water content dependence is much higher than any other studies (expressed in terms of $\sigma \propto C_w^r$, C_w : water content, $r=3.6$ for [100], 3.5 for [010], 2.5 for [001] as compared to $r=0.6-1.0$ in other studies). In terms of absolute values, their results are not far off from those of others when compared at a similar condition (similar water content, temperature), but the first derivatives (activation energy and water content exponent, r) are very different from other studies. Therefore when one extrapolates their result to largely different conditions, the discrepancy will be large. The reason for this large difference is unclear, but I should point out that Poe et al. (2010) determined the water content of their samples only after the conductivity measurements but not before. Consequently, the influence of possible water loss/gain during the measurements was not examined. I suspect that these largely different results are caused by the water loss/gain. It is essential that water content is measured both before and after each conductivity measurement to assure that the influence of water loss/gain is small.

A comparison to geophysical observations

This model explains the known discrepancies between diffusion and conductivity and also provides a way to explain geophysically inferred high and highly anisotropic electrical conductivity in some oceanic asthenosphere (e.g., (Evans et al., 2005; Naif et al., 2013)). High and highly anisotropic conductivity is often attributed to the presence of (aligned) melt (e.g., (Naif et al., 2013; Pommier et al., 2015; Sifré et al., 2014)).

However, it should be emphasized that in order to explain the geophysically observed high and highly anisotropic electrical conductivity of the asthenosphere by partial melting, one would need unusually high volatile content and/or very specific melt geometry. In contrast, a hydrogen model explains the average values and modest anisotropy (a factor of ~ 3 in the horizontal plane) without introducing ad hoc (tunable) parameters.

Based on a model, Pommier et al. (2015) showed that conductivity anisotropy in some deformed partially molten samples is as high as a factor of ~ 100 , and suggested that such a material may explain high anisotropy observed geophysically. The hydrogen model is difficult to explain anisotropy higher than a factor of ~ 10 because it would require unusually strong lattice-preferred orientation that is inconsistent with seismological observations. Therefore if indeed anisotropy were as high as a factor of 50-100, the hydrogen model would have to be rejected. However, such high anisotropy was not often observed in the asthenosphere ((Evans et al., 2005; Naif et al., 2013); also personal communication with Alan Chave and Rob Evans).

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Fig.1

- (a) A schematic diagram showing various H-bearing species in olivine

The Kröger-Vink notation of defects is used: X_Y^Z where X : species, Y : site, Z : effective charge relative to the perfect lattice ($\times$: neutral, $\circ$: +e, $'$: -e).

- (b) A schematic diagram showing the energy levels and the strength of binding for each hydrogen-bearing species. Hydrogen in $(2H)_M^\times$ is trapped in the deep potential well and their mobility is low (and likely crystallographically controlled, i.e., anisotropic). Free proton (or proton in the interstitial site), H° , is only loosely bonded and hence is highly mobile and its diffusion coefficient is not strongly anisotropic. The concentration of each defect is determined their free energy relative to the ground state, ΔG_i . ΔG_i is the smallest for $(2H)_M^\times$, and it has the highest concentration (concentration also changes with chemical conditions; (Nishihara et al., 2008)).

Fig. 2

- (a) A schematic diagram showing the concentration profiles corresponding to isotope diffusion where three different species for each isotope are present

Two materials with different isotopic compositions are in contact, and annealed for a certain time. The concentrations of three species are shown by I, II and III (I', II' III' are isotope variant of each species, e.g., I may be $(2H)_M^\times$, II H_M° , III H°). "I" would correspond to the concentration of $(2H)_M^\times$ (I' to the concentration of $(2D)_M^\times$) etc. "Position" represents the position in a sample ("0" corresponds to the contact surface of two

materials containing different isotopes). The diffusion coefficients of different species are assumed to be different ($D_{I,I'} < D_{II,II'} < D_{III,III'}$) but the diffusion coefficient of the same species with different isotopes is assumed to be the same ($D_I = D_{I'}$, etc.). Concentration is plotted using an arbitrary unit.

(b) The concentration ratios of various species

Blue and red curves are for the case of different diffusion coefficients for different species. Black lines are for a case where all species have a common diffusion coefficient given by $\tilde{D} = \frac{I}{\sum \frac{a_i}{D_i}}$.

When different species diffuse with different diffusion coefficients, then the concentration ratios of species will depend on the position and will have the values that are different from the requirement of the local chemical equilibrium. This would create excess free energy leading to the interaction of each diffusing species. This interaction leads to a situation where diffusion of these species occur with a common diffusion coefficient ($\tilde{D} = \frac{I}{\sum \frac{a_i}{D_i}}$) (Karato, 2013). In this case, the concentration ratios of each species are homogeneous (depend only on temperature and pressure) and the condition of local chemical equilibrium is satisfied.

Fig. 3 A schematic diagram showing the temperature dependence of electrical conductivity (σ) and diffusion coefficient relevant to isotope exchange ($\tilde{D}_{isotope}$)

T: temperature, X: either electrical conductivity or diffusion coefficient relevant to isotope exchange. Arbitrary units are used for T and X. For simplicity, two

mechanisms with different activation energies are considered. Three lines for each correspond to three different crystallographic orientations. I assumed high anisotropy for a mechanism with large activation energy (likely migration of hydrogen in $(2H)_M^\times$).

References

- Dai, L. and Karato, S. (2009) Electrical conductivity of wadsleyite under high pressures and temperatures. *Earth and Planetary Science Letters* 287, 277-283.
- Dai, L. and Karato, S. (2014) High and highly anisotropic electrical conductivity of the asthenosphere due to hydrogen diffusion in olivine. *Earth and Planetary Science Letters* 408, 79-86.
- Du Frane, W.L. and Tyburczy, J.A. (2012) Deuterium-hydrogen interdiffusion in olivine: Implications for point defects and electrical conductivity. *Geochemistry, Geophysics, Geosystems* 13, 10.1029/2011GC003895.
- Evans, R.L., Hirth, G., Baba, K., Forsyth, D.W., Chave, A. and Makie, R. (2005) Geophysical evidence from the MELT area for compositional control on oceanic plates. *Nature* 437, 249-252.
- Glicksman, M.E. (2000) *Diffusion in Solids: Field Theory, Solid-State Principles, and Applications*. John Wiley and Sons, New York.
- Hae, R., Ohtani, E., Kubo, T., Koyama, T. and Utada, H. (2006) Hydrogen diffusivity in wadsleyite and water distribution in the mantle transition zone. *Earth and Planetary Science Letters* 243, 141-148.
- Huang, X., Xu, Y. and Karato, S. (2005) Water content of the mantle transition zone from the electrical conductivity of wadsleyite and ringwoodite. *Nature* 434, 746-749.
- Karato, S. (1990) The role of hydrogen in the electrical conductivity of the upper mantle. *Nature* 347, 272-273.
- Karato, S. (2006) Influence of hydrogen-related defects on the electrical conductivity and plastic deformation of mantle minerals: A critical review, in: Jacobsen, S.D., van der Lee, S. (Eds.), *Earth's Deep Water Cycle*. American Geophysical Union, Washington DC, pp. 113-129.
- Karato, S. (2013) Theory of isotope diffusion in a material with multiple-species and its implications for hydrogen-enhanced electrical conductivity in olivine. *Physics of the Earth and Planetary Interiors* 219, 49-54.
- Karato, S. and Dai, L. (2009) Comments on "Electrical conductivity of wadsleyite as a function of temperature and water content" by Manthilake et al. *Physics of the Earth and Planetary Interiors* 174, 19-21.
- Karato, S. and Wang, D. (2013) Electrical conductivity of minerals and rocks, in: Karato, S. (Ed.), *Physics and Chemistry of the Deep Earth*. Wiley-Blackwell, New York, pp. 145-182.
- Kohlstedt, D.L. and Mackwell, S.J. (1998) Diffusion of hydrogen and intrinsic point defects in olivine. *Zeitschrift für Physikalische Chemie* 207, 147-162.
- Naif, S., Key, K., Constable, S. and Evans, R.L. (2013) Melt-rich channel observed at the lithosphere-asthenosphere boundary. *Nature* 495, 356-359.
- Nishihara, Y., Shinmei, T. and Karato, S. (2008) Effects of chemical environments on the hydrogen-defects in wadsleyite. *American Mineralogist* 93, 831-843.
- Poe, B., Romano, C., Nestola, F. and Smyth, J.R. (2010) Electrical conductivity anisotropy of dry and hydrous olivine at 8 GPa. *Physics of the Earth and Planetary Interiors* 181, 103-111.

- Pommier, A., Leinenweber, K., Kohlstedt, D.L., Qi, C., Garnero, E.J., Mackwell, S.J. and Tyburczy, J.A. (2015) Experimental constraints on the electrical anisotropy of the lithosphere-asthenosphere system. *Nature* 522, 202-206.
- Schmalzried, H. (1995) *Chemical Kinetics of Solids*. VCH, New York.
- Shewmon, P.G. (1989) *Diffusion in Solids*, second edition ed. The Minerals, Metals & Materials Society, Warrendale, PA.
- Sifré, D., Gardés, E., Massuyeau, M., Hashin, L., Hier-Majumder, S. and Gaillard, F. (2014) Electric conductivity during incipient melting in the oceanic low-velocity zone. *Nature* 509, 81-85.
- Stocker, R.L. and Ashby, M.F. (1973) Rheology of the upper mantle. *Review of Geophysics and Space Physics* 11, 391-426.
- Wang, D., Mookherjee, M., Xu, Y. and Karato, S. (2006) The effect of water on the electrical conductivity in olivine. *Nature* 443, 977-980.
- Yang, X. (2012) Orientation-related electrical conductivity of hydrous olivine, clinopyroxene and plagioclase and implications for the structure of the lower continental crust and uppermost mantle. *Earth and Planetary Science Letters* 317/318, 241-250.
- Yoshino, T. and Katsura, T. (2013) Electrical conductivity of mantle minerals: Role of water in conductivity anomalies. *Annual Review of Earth and Planetary Sciences* 41, 605-628.
- Yoshino, T., Matsuzaki, T., Yamashita, S. and Katsura, T. (2006) Hydrous olivine unable to account for conductivity anomaly at the top of the asthenosphere. *Nature* 443, 974-976.

Figure 1

(a)

(b)

Fig. 1 (Karato)

Figure 2

Fig. 2 (Karato)

Figure 3

Fig. 3 (Karato)