

Theory of isotope diffusion in a material with multiple species and its implications for hydrogen-enhanced electrical conductivity in olivine

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ARTICLE INFO

Article history:

Received 1 December 2012
 Received in revised form 22 February 2013
 Accepted 11 March 2013
 Available online 28 March 2013

Keywords:

Electrical conductivity
 Diffusion
 Isotope
 Hydrogen
 Olivine

ABSTRACT

The relationship between isotope diffusion coefficient and electrical conductivity is examined for a material where a dominant charge-carrying atomic species (e.g., hydrogen) is present as various forms with different diffusion coefficients (e.g., two protons trapped at M-site vacancy, one proton trapped at M-site vacancy etc.). It is shown that the isotopic diffusion occurs keeping the concentration ratio of each species fixed as determined by the thermo-chemical environment. Consequently, the isotope diffusion coefficient is the harmonic average of diffusion coefficients of individual species and is dominated by the slowest diffusing species. In contrast, when electric current is carried by charged species, the concentrations of individual species do not change. Therefore, electrical conductivity is related to the arithmetic average of individual diffusion coefficients dominated by the fastest diffusing species. The difference between these two cases can be large when different species have largely different diffusion coefficients. This model provides an explanation for the observed differences between experimental observations on isotopic diffusion (of H-D) and hydrogen-enhanced electrical conductivity and supports a hybrid model of hydrogen-enhanced electrical conduction where electrical conductivity is dominated by the fast moving hydrogen-related species. The species with the largest mobility may change with temperature leading to a change in anisotropy of conductivity. The degree of enhancement of electrical conductivity by hydrogen is high enough to explain most of the geophysically observed electrical conductivity of Earth's upper mantle.

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1. Introduction

Following the suggestion by Karato (1990) that hydrogen may enhance electrical conductivity in olivine, a number of experimental studies have been performed in the last several years to test this hypothesis. These studies have largely confirmed the original hypothesis, but details are still debated including the magnitude of this effect and the atomic mechanisms by which hydrogen enhances electrical conductivity (for review see Karato and Wang (2013); Yoshino (2010)).

In the first paper where the important role of hydrogen in electrical conductivity was suggested, Karato (1990) used the chemical diffusion coefficient determined by Mackwell and Kohlstedt (1990) and calculated electrical conductivity for a range of hydrogen content. Chemical diffusion of hydrogen involves diffusion of hydrogen together with the diffusion of another charge-compensating species, and hence this method would be valid only when the diffusion of charge-compensating species is faster than the intrinsic diffusion coefficient of hydrogen (Kohlstedt and Mackwell, 1998). The charge-compensating diffusing species is either M-site vacan-

cies or electron holes, both of which have high diffusion coefficients and hence this assumption is likely justified (Kohlstedt and Mackwell, 1998).

However, already in the early studies such as (Wang et al., 2006), it was recognized that the electrical conductivity calculated from the diffusion coefficients of hydrogen gives systematically smaller values than actually measured conductivity. Also the activation energy of hydrogen-assisted conductivity (~ 70 – 90 kJ/mol) is much smaller than that of diffusion (~ 140 – 150 kJ/mol) (Dai and Karato, 2009b; Hae et al., 2006; Yoshino, 2010). Such differences have been confirmed by the recent study of isotope diffusion of hydrogen and deuterium in olivine (Du Frane and Tyburczy, 2012) (Fig. 1). The discrepancy includes not only the discrepancy in the magnitude of conductivity and activation enthalpy (Fig. 1a) but also the nature and magnitude of anisotropy (Fig. 1b).

Any viable model of hydrogen-enhanced electrical conductivity must explain these major discrepancies. Based on these observations as well as the observed dependence of conductivity on water content (water fugacity), (Karato, 2006) concluded that a simple model assuming a single hydrogen-related species is not appropriate and proposed a hybrid model where the role of multiple hydrogen-related species is emphasized. In contrast, from the same observation,

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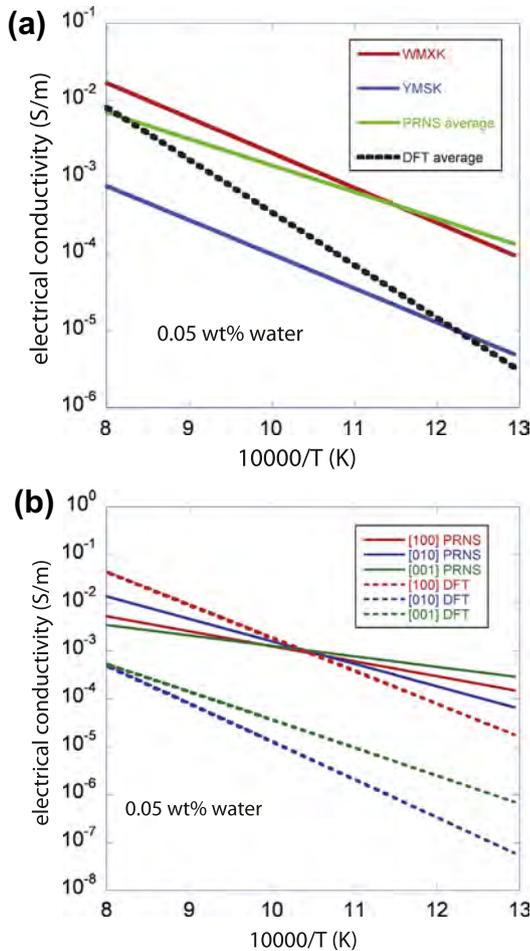


Fig. 1. A comparison of measured electrical conductivity with the conductivity calculated from isotope diffusion coefficients. The comparison is made for the water content of 0.05 wt.% to minimize the influence of extrapolation (most of measurements in the literature were made at or near this water content). Data source, DFT: (Du Frane and Tyburczy, 2012), PRNS: (Poe et al., 2010), WMXK: (Wang et al., 2006), YMSK: (Yoshino et al., 2009)). The water content for each measurement corresponds to those determined by SIMS (when FTIR with (Paterson, 1982) calibration is used, a correction factor of 3 was applied). (a) A comparison of average conductivity. All conductivity data show much lower activation energy than that of isotope diffusion. The results by WMXK agree well with those by PRNS. The results by YMSK show much lower conductivity than these. (b) A comparison of conductivity including anisotropy. Anisotropy of conductivity reported by Poe et al. (2010) changes with temperature and is markedly different from anisotropy calculated from the isotope diffusion data reported by Du Frane and Tyburczy (2012).

Du Frane and Tyburczy (2012) concluded that the degree to which hydrogen enhances electrical conductivity is not as large as (Wang et al., 2006) and (Dai and Karato, 2009a) showed, and they argued that a hybrid model presented by Karato (2006) is inconsistent with their observation.

Problems with a simple single-species model have been discussed in several previous papers where a hybrid model of conductivity was presented to explain such discrepancies (Karato, 2006; Karato and Wang, 2013). However, atomistic mechanisms to cause these differences were not explained very clearly in the previous studies. Given the new experimental work by Du Frane and Tyburczy (2012) that clearly demonstrated the discrepancies between isotope diffusion and conductivity measurements, and given their discussion against a hybrid model of electrical conductivity, it seems appropriate to provide a theoretical analysis of isotope diffusion to understand the causes of these discrepancies. In this paper, I will examine the microscopic physics of isotope exchange

between two materials where a given atomic species (e.g., hydrogen) occurs in a multiple forms. I will show that direct correlation between isotope diffusion coefficient and electrical conductivity is broken down in such a case if a given atomic species in different forms have largely different diffusion coefficients. Consequently, the direct comparison of electrical conductivity calculated from isotope diffusion coefficients and actual electrical conductivity is not justified in these materials.

2. Theory

When electric current is carried by charged species, electrical conductivity is related to the diffusion coefficients of relevant species. Such a relation is given by the Nernst–Einstein relationship (e.g., Mott and Gurney, 1940), viz.,

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

where σ is electrical conductivity, f_i is a non-dimensional factor of order unity, q_i is the electrical charge (relative to the vacuum), D_i is the diffusion coefficient, C_i is the concentration of the i -th species, and RT has usual meaning. This relation would imply that once one knows the concentration and (self) diffusion coefficient of all relevant species, one can calculate electrical conductivity.

The relation (1) is valid only when summation over i is made for all relevant species. When a given atomic species, say hydrogen, occurs in several different forms (e.g., two protons at M-site, one proton at M-site, free proton etc.) then summation must be made for all of these species. As I will show in this paper, in a material where a given species (e.g., hydrogen) occurs in various forms, the isotope exchange involves strong interaction of various species and consequently, isotope diffusion coefficient does not directly represent the self diffusion coefficient of any atomic species but rather corresponds to some average of individual diffusion coefficients. Consequently the relation between individual diffusion coefficients and isotopic diffusion coefficient needs to be known in order to understand the relationship between isotopic diffusion coefficient and electrical conductivity.

3. Theory

Experimental observations summarized by Karato (2006); Karato and Wang (2013); Nishihara et al. (2008) suggest that hydrogen in these materials ((Mg,Fe)₂SiO₄) is dissolved in multiple forms including (2H)_M[×] (two protons at M-site vacancy), H_M⁺ (one proton at M-site vacancy) and H⁺ (“free” proton) (for deuterium, (2D)_M[×], D_M⁺, D⁺). Hydrogen in each of these species has different chemical bonding with its surroundings, and therefore likely has different mobility. These species are created by the ionization reaction,



The concentrations of these defects may also be affected by the presence of other charged defects such as the M-site vacancy, V_M^{''} (Karato, 2008). At equilibrium, the concentration ratio of each species is determined by the physico-chemical environment (temperature, pressure, the fugacity of water and of oxygen, and oxide activity) (Nishihara et al., 2008).

In an isotope exchange experiment, one brings two crystals with different isotopic compositions (H/D ratios) into contact (Fig. 2). When multiple species are present, concentration gradient must be present for each species that varies as a function of position. Consequently, each species will diffuse driven by the concentration gradient, and the diffusion flux should be proportional to the diffusion coefficient of each species.

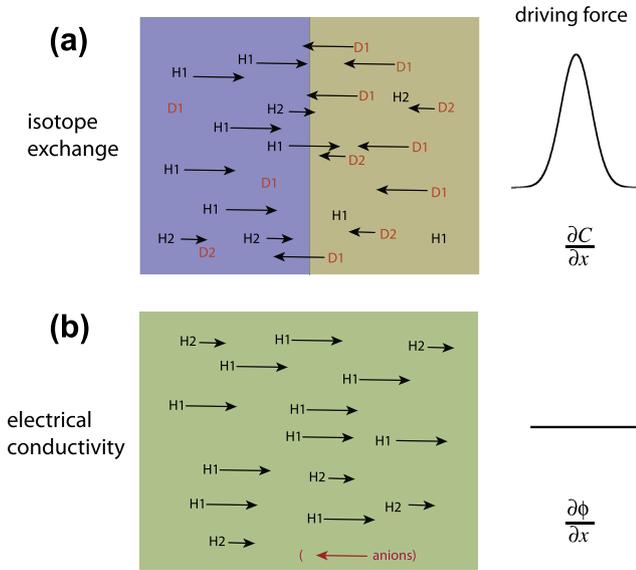


Fig. 2. Schematic diagrams showing (a) the processes of isotope exchange and (b) the process of electrical conduction. H indicates hydrogen-bearing species and D indicates deuterium-bearing species (e.g., H1, H2 denote different hydrogen-bearing species such as $(2H)_M^*$ and H^*). There are multiple species for both hydrogen and deuterium that have different diffusion coefficients. In case of isotope diffusion, each species moves driven by concentration gradient that changes with position, and consequently, if each species moves freely without interaction, the concentration ratio would change. This creates excess free energy because the concentration ratio should be determined by thermodynamic environment at equilibrium. Consequently, there will be interaction among diffusing species in isotope diffusion with multiple-species. In contrast, when electric current flows, driving force is uniform and the concentration of each species does not change. Therefore there is no direct interaction among different species.

The concentration gradient, $-\frac{\partial C_j}{\partial x}$, in this case changes with position (for the error function distribution of concentration, $\frac{\partial C_j}{\partial x} \propto \exp(-\frac{x^2}{4Dt_j})$) and therefore the flux of each species changes with position. This causes a change in the concentration of each species differently ($\frac{\partial C_j}{\partial t} = -\frac{\partial}{\partial x} J_j \neq 0$, see Fig. 2). This would violate various constraints including the charge neutrality and the thermo-chemically determined concentration ratios. Therefore there must be some interactions among various diffusing species to assure that these constraints are satisfied.

In addition to the obvious constraint of the charge neutrality, let us consider the constraint of concentration ratios of various species. Chemical reactions such as the one described by Eq. (2) impose that, at equilibrium, the concentration ratios of various species are determined by the thermo-chemical conditions through the law of mass action. Let us consider how such a requirement may affect diffusion. Because isotope exchange of one atomic species, e.g., hydrogen and deuterium, occurs without affecting the concentrations (i.e., chemical potentials) of other species such as Mg (magnesium) or Si (silicon), I will focus on a single couple of isotopic species such as hydrogen and deuterium in isolation. In these cases, the total concentration of hydrogen and deuterium is fixed,

$$C_H + C_D = C_{total} \quad (3)$$

where $C_{H(D)}$ is hydrogen (deuterium) concentration (C_{total} is the total concentration of hydrogen and deuterium). For each species (H or D), there are several forms in which they occur (e.g., $(2H, 2D)_M^*$, $(H, D)_M^*$, $(H, D)^*$), so that

$$C_{j,H(D)} = \alpha_{j,H(D)} C_{H(D)} \quad (4)$$

where $\alpha_{j,H(D)}$ is the fraction of hydrogen (or deuterium) with the j -th form (such as $(2H)_M^*$), and of course $\sum_j \alpha_{j,H(D)} = 1$. At equilibrium,

these coefficients do not depend on the isotopic mass to the first approximation, so that $\alpha_{j,H}^0 \approx \alpha_{j,D}^0 = \alpha_j^0$ with $\sum_j \alpha_j^0 = 1$. Since the concentration of hydrogen-bearing species is related to that of deuterium-bearing species by the relation (3), I need only to consider the concentration of hydrogen-bearing species in the following.

The local concentration of the j -th species is controlled by the spatial variation in diffusional flux, $\frac{\partial}{\partial x} J_j$, as well as the change in the concentration caused by the deviation of the concentration from the equilibrium concentration. Therefore the net change in the concentration of the j -th species is given by

$$\frac{\partial C_j}{\partial t} = -\frac{\partial}{\partial x} J_j - \frac{1}{\tilde{\tau}_j} (C_j - C_j^0) \quad (5)$$

where C_j is the concentration of the j -th species (the j -th hydrogen-containing species), C_j^0 is its equilibrium value corresponding to the reaction such as (2), and $\tilde{\tau}_j$ is the relaxation time for the change in the concentration associated with such reactions. The first term in the right-hand-side represents the change in the concentration caused by the material flux, and the second term in the right-hand-side corresponds to the ‘‘creation’’ or ‘‘destruction’’ of the j -th species by the transition of species through reaction (2). In order to evaluate the role of these two processes, let us consider a simple case where the flux of the species is caused solely by the concentration gradient. In that case, Eq. (5) is reduced to

$$\frac{\partial C_j}{\partial t} = D_j \frac{\partial^2 C_j}{\partial x^2} - \frac{1}{\tilde{\tau}_j} (C_j - C_j^0) \quad (6)$$

where D_j is the diffusion coefficient of the j -th species. Assuming the solution with a form $C_j - C_j^0 \propto \exp(-\frac{t}{\tau_j^{local}}) \cos \frac{\pi x}{l}$ one obtains

$$\tau_j^{local} = \frac{\tilde{\tau}_j}{1 + \frac{\pi^2 D_j \tilde{\tau}_j}{l^2}} \quad (7)$$

where τ_j^{local} is the characteristic time of change in concentration at a fixed position x (the local characteristic time of change in concentration of the j -th species). The process of the change in the concentration of atomic species at a given site is similar to the process of the change in the atomic concentration among different sites associated with the Snoek peak of anelasticity. In both cases, the key process is the motion of an atomic species between two different sites caused by the difference in free energies at these sites. Therefore the characteristic time for such a reaction can be calculated using a theory for the Snoek peak (Nowick and Berry, 1972) and is given by

$$\tilde{\tau}_j \approx \frac{a^2}{\pi^2 D_j} \quad (8)$$

where a is the distance between atomic sites ($a \sim 1$ nm) and D_j is the self diffusion coefficient of the j -th species. Consequently,

$$\tau_j^{local} = \frac{\tilde{\tau}_j}{1 + \frac{\pi^2 D_j \tilde{\tau}_j}{l^2}} = \frac{\tilde{\tau}_j}{1 + \frac{a^2}{l^2}} \quad (9)$$

In comparison, the time-scale of isotopic diffusion of a distance l is given by

$$\tau_j^{isotope} \approx \frac{l^2}{\pi^2 D_j} \quad (10)$$

where l is the distance of diffusion ($l \sim 100$ μm ; (Du Frane and Tyburczy, 2012)). Therefore

$$\frac{\tau_j^{isotope}}{\tau_j^{local}} \approx \left(\frac{l}{a}\right)^2 \gg 1 \quad (11)$$

and hence $\tau_j^{local} \approx \tilde{\tau}_j$.

This means that the local equilibrium must be well achieved during an isotope diffusion experiment. Consequently, the isotope diffusion in these cases occurs under the conditions where the concentration ratio is fixed. This is similar to the diffusion creep in a compound where diffusion of various charged species occurs where charge neutrality and fixed stoichiometric ratio conditions are satisfied (Karato, 2008). Diffusion problem under such conditions can be analyzed by invoking the internal electric field (the Nernst field), ϕ , viz.,

$$J_j = -\frac{D_j C_j}{RT} \left(\frac{RT \partial \log C_j}{\partial x} + q_j \frac{\partial \phi}{\partial x} \right) \quad (12)$$

where q_j is the electric charge of the j -th species.

The charge neutrality condition reads,

$$\sum_j q_j C_j = C \sum_j q_j \alpha_j = 0 \quad (13)$$

where C is $C_{H(D)}$ (I omitted the suffix H or D for simplicity). Also because the concentration of each species is determined locally by the thermo-chemical equilibrium, the flux must satisfy,

$$J_j = \alpha_j J \quad (14)$$

where J is the flux of a group of molecule. Note that relations (13) and (14) imply that no net current condition is satisfied ($I = \sum_j q_j J_j = 0$).

Combining relations (12) and (14), and using the charge neutrality condition (i.e., (13)), and operating $\sum \alpha_i$, one can eliminate the electrostatic potential and obtains

$$J = -\frac{1}{\sum_j \frac{\alpha_j}{D_j}} \frac{\partial C}{\partial x} \quad (15)$$

Because this equation expresses the relation between the total flux of hydrogen (J) and the gradient of total concentration of hydrogen ($\frac{\partial C}{\partial x}$) during the isotopic exchange, one can define the effective diffusion coefficient relevant to isotopic exchange as,

$$D^{\text{isotope}} = \frac{1}{\sum_j \frac{\alpha_j}{D_j}} \quad (16)$$

It is seen that the isotope diffusion coefficient is given by the harmonic average of diffusion coefficients of relevant species weighted by their concentration. Consequently, among various diffusing species ($(2H)_M^\times, H'_M, H'$ in case of H/D diffusion in $(Mg, Fe)_2\text{-SiO}_4$), it is the species with the largest $\frac{\alpha_j}{D_j}$, i.e., the slowest diffusing species with a high concentration, that dominates isotope diffusion, most likely $(2H)_M^\times$.

The situation in electrical conductivity is different and simpler. When electric field is applied, all charged species migrate driven by the generalized force $-q_j \frac{\partial \phi}{\partial x}$. Because this force is homogeneous (independent of x) through a sample, $\frac{\partial}{\partial x} J_j = 0$ in Eq. (5) and the concentration of each species does not change with time when electric current flows. Consequently, there is no interaction among diffusing species as far as the current is homogeneous (this is not the case when electric charge is built up at an electrode) and diffusion coefficients in Eq. (1) are simply the diffusion coefficients of individual species. Therefore among various species, the one that gives the largest $q_j^2 D_j \alpha_j$ will dominate the conductivity.

4. Discussion

The theoretical consideration presented in this paper shows that when various species are involved in isotopic diffusion, then the species that has the large concentration and the smallest diffusion coefficient (i.e. the largest $\frac{\alpha_j}{D_j}$) controls the rate of isotopic exchange. In case of hydrogen in olivine or wadsleyite, this is likely the dominant defect $(2H)_M^\times$ that is most abundant and likely has

the slow mobility because protons in this defect are strongly bonded to the matrix crystal (compared to other defects such as free proton, H'). Therefore the isotope diffusion coefficient essentially corresponds to the diffusion coefficient of $(2H)_M^\times$. In chemical diffusion, another charge compensating species (such as M-site vacancy, V'_M , or electron hole) must also diffuse and the diffusion coefficients in Eq. (7) should include the diffusion coefficient of these species. However, diffusion of these charge-compensating species is fast (Kohlstedt and Mackwell, 1998) and chemical diffusion and isotopic diffusion coefficient should be similar. In fact, both the absolute values and the activation energies of these diffusion coefficients agree reasonably well (Du Frane and Tyburczy, 2012; Hae et al., 2006; Kohlstedt and Mackwell, 1998). In contrast, electrical conductivity is dominated by the species that has the largest $q_j^2 D_j \alpha_j$, i.e., the species that has the large diffusion coefficient. In general, the activation energy of faster diffusing species is smaller than that of the slower diffusing species. And in fact, the activation energy of electrical conductivity due to hydrogen in olivine and wadsleyite is ~ 70 – 90 kJ/mol that is substantially smaller than that of isotope diffusion (~ 140 – 150 kJ/mol).

These predictions from the present model are exactly what have been observed in these materials where hydrogen is present in various forms. Therefore the results of isotope diffusion of H/D in olivine determined by Du Frane and Tyburczy (2012) provide a strong support for a hybrid model by Karato (2006) where electrical conductivity in olivine and other minerals caused by hydrogen is considered to be due mainly to the diffusion of minor but faster diffusing species such as H' . The hybrid model of hydrogen-assisted electrical conductivity also explains a diverse range of observations including the systematic difference in normalized conductivity among the different groups of hydrogen-bearing minerals (Karato and Wang, 2013) and the dependence of hydrogen-enhanced electrical conductivity on oxygen fugacity (Dai and Karato, 2009b) (in the simple model where $(2H)_M^\times$ controls the conductivity, conductivity should be independent of oxygen fugacity). In contrast, if one assumes that all hydrogen-related species diffuse equally or that only one hydrogen-related species is present (e.g., Du Frane and Tyburczy, 2012; Yoshino, 2010), then the difference in activation energy between isotope diffusion and electrical conductivity and the dependence of conductivity on oxygen fugacity as observed for wadsleyite (Dai and Karato, 2009b) cannot be explained.

I conclude that electrical conductivity in olivine and wadsleyite is enhanced by a hydrogen-bearing fast moving species but the kinetics of isotopic exchange is controlled by the diffusion of the slowest diffusing species. Consequently, the hydrogen-enhanced conductivity in olivine must be higher than the hydrogen-enhanced conductivity calculated from the H-D isotope diffusion coefficients. The degree of enhancement is enough to explain a majority of the geophysical observations (Dai and Karato, 2009a; Karato, 2011) and there is no need for partial melting to explain the observed electrical conductivity in most of the mantle.

Given the good agreement of predictions of the theoretical model with a range of observations summarized above, it is puzzling that some of the experimental data on electrical conductivity agree reasonably well with the simple model in which the role of multiple species is not considered. These are the data by Yoshino et al. (2009) (Du Frane and Tyburczy (2012) argued that Poe et al. (2010)'s data also agree with their results, but a more direct comparison shows that Poe et al. (2010)'s results are very different from Du Frane and Tyburczy (2012) and similar to the results by Wang et al. (2006); see Fig. 1a, b). The reason for this puzzling observation is not entirely clear. Unlike their earlier work (Yoshino et al., 2006) where only one frequency was used, Yoshino et al. (2009) used the impedance spectroscopy and therefore this should not be the cause for low conductivity in these studies. One possibility is the pressure effects on conductivity, because Yoshino et al.

(2009) measured the conductivity at 10 GPa compared to 2 GPa where the measurements by Du Frane and Tyburczy (2012) was made. However, the measurements by Poe et al. (2010) were made at 8 GPa and the results agree well with those of Wang et al. (2006) that were obtained at 4 GPa. It should be noted, however, that although the agreement in the magnitude of conductivity between Yoshino et al. (2009) and Du Frane and Tyburczy (2012) is “good”, the activation energies determined by Yoshino et al. (2009) (~90 kJ/mol) differ significantly from that of isotope diffusion (140–150 kJ/mol) and the agreement is only in the limited temperature range. Therefore the “agreement” could be fortuitous.

An interesting, although somewhat speculative, prediction of this model is that at high temperatures, the mobility of $(2H)_M^{\times}$ will become higher than that of H^{\cdot} (or H'_M), so that the activation energy of conductivity will increase. This implies that the direct extrapolation of low temperature data such as Wang et al. (2006) would underestimate the conductivity. If one uses the results shown in Fig. 1a, this critical temperature is estimated to be ~1400–1500 K. Because this temperature is close the temperature in the asthenosphere (~1500–1600 K), the influence of this mechanism change will not be very large (a factor of ~2 or so). Fig. 3 shows electrical conductivity of olivine aggregate as a function of temperature and water content including this possible transition in hydrogen-conduction mechanism. The electrical conductivity by this mechanism is calculated from the isotope diffusion coefficients and all the parameters are given in Table 1.

A useful test to evaluate this new model is to determine the dependence of hydrogen-enhanced conductivity in olivine on oxygen fugacity. For a hybrid model, at the low temperature regime where minority defects such as H^{\cdot} (or H'_M) control the conductivity, hydrogen-enhanced conductivity should decrease with oxygen fugacity (e.g., Dai and Karato, 2009b; Nishihara et al., 2008) whereas if the dominant hydrogen defect, $(2H)_M^{\times}$ controls the conductivity, then electrical conductivity will be independent of oxygen fugacity. In the model by Du Frane and Tyburczy (2012) and Yoshino (2010), $(2H)_M^{\times}$ always controls conductivity and hence conductivity is always independent of oxygen fugacity. In the hybrid model, in contrast, conductivity will decrease with oxygen

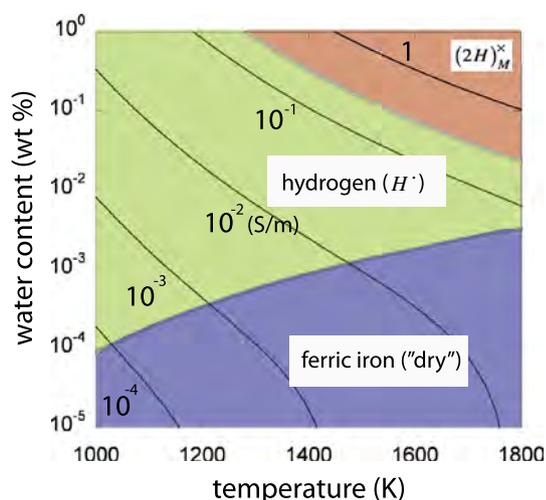


Fig. 3. Electrical conductivity mechanism map of olivine as a function of water content and temperature. The results are applicable to pressure of 2–4 GPa (shallow asthenosphere). Oxygen fugacity is assumed to be close to Ni–NiO buffer. Three mechanisms are considered: (1) ferric iron conduction (“dry” olivine), (2) conduction by diffusion of $(2H)_M^{\times}$, (3) conduction by diffusion of H^{\cdot} (or H'_M). Random orientation is assumed. Thin curves are the constant conductivity lines corresponding to the given temperature and water content. Conductivity anisotropy is substantially large in mechanism (2), i.e., at high temperature and water-rich environment (i.e., at high conductivity).

Table 1

Parameters for electrical conductivity of polycrystalline olivine. The following form is assumed: $\sigma = \sigma_0 \left(\frac{C_w}{C_{w0}}\right)^r \exp\left(-\frac{H^*}{RT}\right)$ where C_w is water content, H^* is activation enthalpy, r is a non-dimensional constant (C_{w0} is a reference water content and is 0.01 wt.%). Oxygen fugacity is assumed to be at Ni–NiO buffer. The data are at 2 GPa for mechanism (2) (i.e., conduction by $(2H)_M^{\times}$) and at 4 GPa for mechanism (3) (conduction by H^{\cdot} or H'_M). Ferric iron (“polaron”) conduction is not sensitive to pressure (Xu et al., 2000), but pressure effects on hydrogen-conduction is not known for olivine. These results are applicable to the shallow upper mantle. The data are from Du Frane and Tyburczy (2012) and Karato and Wang (2013). Numbers in the parenthesis indicates errors in one standard deviation.

	σ_0 (S/m)	r	H^* (kJ/mol)
Ferric iron (“small polaron”)	$10^{2.5(0.2)}$	–	154 (5)
Hydrogen ($(2H)_M^{\times}$)	$10^{3.0(1.4)}$	1 (0.1)*	140 (30)
Hydrogen (H^{\cdot} or H'_M)	$10^{1.6(0.4)}$	0.62 (0.2)	87 (5)

* Assumed value based on the solubility data by Kohlstedt et al. (1996).

fugacity in the low-temperature regime and will become independent of oxygen fugacity at high-temperature regime. Activation energy will also change with temperature in the hybrid model.

Finally, I should note that because controlling atomic species are different between isotope diffusion and electrical conductivity, there is no reason to believe that the nature of anisotropy is the same between these two properties. In fact, anisotropy in isotope diffusion coefficients reported by Du Frane and Tyburczy (2012) is markedly larger than the anisotropy of conductivity reported by Poe et al. (2010) under the conditions of the measurements and also the anisotropy in the activation energy is different between isotope diffusion and conductivity (Fig. 1b). However, if conduction mechanism under the asthenosphere conditions changes to the one by $(2H)_M^{\times}$, then anisotropy in hydrogen-enhanced electrical conductivity will be similar to the anisotropy in isotope diffusion and will be large.

Acknowledgment

This study was partly supported by grants from NSF. Reviews by anonymous reviewers helped clarify the presentation.

References

- Dai, L., Karato, S., 2009a. Electrical conductivity of orthopyroxene: implications for the water content of the asthenosphere. *Proceedings of the Japan Academy* 85, 466–475.
- Dai, L., Karato, S., 2009b. Electrical conductivity of wadsleyite under high pressures and temperatures. *Earth and Planetary Science Letters* 287, 277–283.
- Du Frane, W.L., Tyburczy, J.A., 2012. Deuterium–hydrogen interdiffusion in olivine: implications for point defects and electrical conductivity. *Geochemistry, Geophysics, Geosystems* 13. <http://dx.doi.org/10.1029/2011GC003895>.
- Hae, R., Ohtani, E., Kubo, T., Koyama, T., Utada, H., 2006. Hydrogen diffusivity in wadsleyite and water distribution in the mantle transition zone. *Earth and Planetary Science Letters* 243, 141–148.
- 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., 2008. *Deformation of Earth Materials: Introduction to the Rheology of the Solid Earth*. Cambridge University Press, Cambridge.
- Karato, S., 2011. Water distribution across the mantle transition zone and its implications for global material circulation. *Earth and Planetary Science Letters* 301, 413–423.
- Karato, S., 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., Keppler, H., Rubie, D.C., 1996. Solubility of water in the α , β and γ phases of $(Mg, Fe)_2SiO_4$. *Contributions to Mineralogy and Petrology* 123, 345–357.
- Kohlstedt, D.L., Mackwell, S.J., 1998. Diffusion of hydrogen and intrinsic point defects in olivine. *Zeitschrift für Physikische Chemie* 207, 147–162.
- Mackwell, S.J., Kohlstedt, D.L., 1990. Diffusion of hydrogen in olivine: implications for water in the mantle. *Journal of Geophysical Research* 95, 5079–5088.

- Mott, N.F., Gurney, R.W., 1940. *Electronic Processes in Ionic Crystals*. Dover, New York.
- Nishihara, Y., Shinmei, T., Karato, S., 2008. Effects of chemical environments on the hydrogen-defects in wadsleyite. *American Mineralogist* 93, 831–843.
- Nowick, A.S., Berry, B.S., 1972. *Anelastic Relaxation in Crystalline Solids*. Academic Press, San Diego.
- Paterson, M.S., 1982. The determination of hydroxyl by infrared absorption in quartz, silicate glass and similar materials. *Bulletin Mineralogie* 105, 20–29.
- Poe, B., Romano, C., Nestola, F., 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.
- Wang, D., Mookherjee, M., Xu, Y., Karato, S., 2006. The effect of water on the electrical conductivity in olivine. *Nature* 443, 977–980.
- Xu, Y., Shankland, T.J., Duba, A.G., 2000. Pressure effect on electrical conductivity of mantle olivine. *Physics of the Earth and Planetary Interior* 118, 149–161.
- Yoshino, T., 2010. Laboratory electrical conductivity measurement of mantle minerals. *Surveys in Geophysics* 31, 163–206.
- Yoshino, T., Matsuzaki, T., Shatskiy, A., Katsura, T., 2009. The effect of water on the electrical conductivity of olivine aggregates and its implications for the electrical structure of the upper mantle. *Earth and Planetary Science Letters* 288, 291–300.
- Yoshino, T., Matsuzaki, T., Yamashita, S., Katsura, T., 2006. Hydrous olivine unable to account for conductivity anomaly at the top of the asthenosphere. *Nature* 443, 974–976.