

Electrical conductivity of minerals and rocks

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SUMMARY

Electrical conductivity of most minerals is sensitive to hydrogen (water) content, temperature, major element chemistry and oxygen fugacity. The influence of these parameters on electrical conductivity of major minerals has been characterized for most of the lower crust, upper mantle and transition zone minerals. When the results of properly executed experimental studies are selected, the main features of electrical conductivity in minerals can be interpreted by the physical models of impurity-assisted conduction involving ferric iron and hydrogen-related defects. Systematic trends in hydrogen-related conductivity are found among different types of hydrogen-bearing minerals that are likely caused by the difference in the mobility of hydrogen. A comparison of experimental results with geophysically inferred conductivity shows: (1) Electrical conductivity of the continental lower crust can be explained by a combination of high temperature, high (ferric) iron content presumably associated with dehydration. (2) Electrical conductivity of the asthenosphere can be explained by a modest amount of water ($\sim 10^{-2}$ wt% in most regions, less than 10^{-3} wt% in the central/western Pacific). (3) Electrical conductivity of the transition zone requires a higher water content ($\sim 10^{-1}$ wt% in most regions, $\sim 10^{-3}$ wt% in the southern European transition zone, ~ 1 wt% in the East Asian transition zone). The majority of observations including those on the lower crust and the asthenosphere can be interpreted without partial melting or any fluids.

However, experimental studies on electrical conductivity of lower mantle minerals are incomplete and it is not known if hydrogen enhances the conductivity of lower mantle minerals or not. Some discussions are also presented on the electrical conductivity in other planetary bodies including the Moon and Mars.

INTRODUCTION

Seismic wave velocities and electrical conductivity are among the physical properties that can be estimated from geophysical remote sensing techniques. However, inferring electrical conductivity is more challenging and subject to larger uncertainties than for seismic wave velocities (see a Chapter by A. Schultz). Consequently, although the basic framework of the inference of electrical conductivity from electromagnetic induction has long been known (see e.g., (Banks, 1969, Rikitake, 1966)), progress in the study of electrical conductivity and its applications to Earth's interior have been slow until recently.

It might seem that because the resolution of electrical conductivity is much lower than that of seismic wave velocities, studies of electrical conductivity have secondary importance compared to the study of seismic wave velocities and elasticity. However, the sensitivity of these two properties to various parameters is different and the use of these observables is complementary. For instance, seismic wave velocities are highly sensitive to the major element chemistry and crystal structure (see a Chapter by Murakami, Tsuchiya and Kawai) but relatively insensitive to water content. In contrast, electrical conductivity is highly sensitive to water content and relatively insensitive to other factors as we will show in this paper. Therefore in order to infer the water distribution, electrical conductivity plays a primary role (see also (Karato, 2011)). The approaches using these two observables are complementary and by using both of them, one can get a detailed knowledge of composition and evolution of Earth.

Hydrogen (water) has important influence on rheological properties (e.g., (Karato and Jung, 2003, Mei and Kohlstedt, 2000)) and melting relationship (e.g., (Kushiro *et al.*,

1968, Inoue, 1994)) that control the dynamics and evolution of Earth and other terrestrial planets (see also Chapters by Keppeler, Iwamori, van Keken and Karato). In some regions of the mantle such as the highly depleted lithosphere, there is essentially no water (less than a few wt ppm) whereas in certain regions ~1 wt % of water is inferred to be present (Stolper and Newman, 1994). Therefore the range of water content in Earth's mantle spans more than four orders of magnitude. However, these estimates are from petrological studies and the spatial distribution of water is poorly constrained. Consequently, if one can infer the water content with an uncertainty of a factor of ~2, this will be a major improvement of our understanding of water distribution and hence the dynamics and evolution of Earth (and other planets)¹. According to a model by (Karato, 1990), the electrical conductivity is proportional to the water content (minor revision is needed for some minerals as we will discuss later), so if one can infer electrical conductivity within a factor of ~2 and if the influence of other factors is small or properly corrected, then one can make an important advancement in our understanding of water distribution in the current Earth's mantle. Consequently, a large number of papers have been published on this topic after 1990.

However, the measurements and the interpretation of experimental results on electrical conductivity are not straightforward, particularly those on samples with hydrogen (water), and there have been some confusions in the community. As a result, somewhat different results have been published and largely different models were proposed on the distribution of hydrogen from electrical conductivity. For example, (Huang *et al.*, 2005, Karato, 2011) proposed a relatively high water content (~0.1 wt %)

¹ The uncertainties in the geochemical estimate of water content are similar (e.g., Hirschmann (1006)).

in the transition zone, whereas (Yoshino *et al.*, 2008a, Yoshino, 2010) proposed a dry (water-free) transition zone. Therefore it seems important to review the basic physics of electrical conductivity, including the technical issues on the experimental methods, to evaluate the validity of different results and models.

In this paper, we will first review the basic physics of electrical conductivity and point defects in minerals and discuss some issues on the experimental studies and their interpretation. Then important experimental results will be summarized and the microscopic mechanisms of electrical conduction in minerals will be reviewed. Finally, the results will be applied to infer the physical and chemical state of Earth and planetary (mostly the Moon) interiors from electrical conductivity.

MICROSCOPIC PHYSICS OF ELECTRICAL CONDUCTIVITY

Some fundamentals

When an electric field is applied, electrical current flows in materials due to the motion of charged particles (electrons and/or ions). Therefore the electrical conductivity is proportional to the number density of charged particles and their mobility. In most cases there is a linear relationship between the electrical current and the applied electric field E (the Ohm's law), and the proportional coefficient is the electrical conductivity, $I = \sigma E$. Therefore one has

$$\sigma = |q|n\mu \quad (1)$$

where q is the charge of the particle that carries the current, n is the number density of the particle and $\mu = v / E$ is the mobility where v is the drift velocity of the particle. When there are multiple charged species that carry the electric current, equation (1) should be modified to $\sigma = \sum_i |q_i| n_i \mu_i$ (each quantity with a suffix i refers to a quantity for the i -th species) and the electrical conductivity is dominated by the motion of charged species that has the highest $|q_i| n_i \mu_i$.

In metals, the number of charge carriers is fixed (=number of free electrons), and the temperature dependence of electrical conductivity comes only from that of mobility. The mobility of free electrons is controlled by the scattering by phonons and weakly dependent on temperature, $\mu \propto \frac{1}{T}$ (T : temperature) (e.g., (Kittel, 1986)). Most of minerals are semi-conductors or insulators where mobile charged particles are present only by thermal activation and their concentrations are highly sensitive to the amount of impurities as well as temperature. In addition, the mobility of charge carriers in minerals is often highly sensitive to temperature. Therefore the electrical conductivity in minerals is not only sensitive to temperature but also sensitive to parameters that control the activities of impurities including water and oxygen fugacity. Consequently, there is a potential to infer the distribution of these chemical factors (as well as temperatures) from the study of electrical conductivity that are otherwise difficult to infer. In the following, we will first review the fundamentals of mechanisms of electrical conduction in minerals, and review some experimental issues, and then summarize the results of laboratory studies and their interpretation and applications.

Electrical conductivity and impurities

Intrinsic conductivity

A typical silicate or oxide mineral free from transition metals such as MgO (periclase) or Mg_2SiO_4 (forsterite) is an insulator in which all electrons are strongly bound to the atomic nuclei. In these materials, all electrons belong to the filled bands and they become mobile only when an electron is removed from the filled valence band to the empty conduction band by thermal activation (**Fig. 1**). The creation of these mobile electrons and holes can be described by



where e' is electron (with excess negative charge) and h^{\bullet} is hole (with positive effective charge). From the law of mass action and the requirement of charge neutrality by these two defects, one has $[e'] = [h^{\bullet}] \propto \exp\left(-\frac{E_g}{2RT}\right)$ where $[x]$ denotes the concentration of a species x . Using this relation, and considering that the density of state of electrons follows the Fermi statistics, the electrical conductivity can be given by (e.g., (Ziman, 1960, Kittel, 1986)),

$$\sigma = 2e^2 \left(\frac{2\pi kT}{h^2}\right)^{3/2} \cdot (m_e m_h)^{3/4} \cdot (\mu_e + \mu_h) \cdot \exp\left(-\frac{E_g}{2RT}\right) \quad (3)$$

where k is the Boltzmann constant, R is the gas constant ($R=N_A k$, N_A : the Avogadro number), h is the Planck constant, $m_{e,h}$ is the effective mass of electron or hole

respectively, $\mu_{e,h}$ is the mobility of electron or hole, and E_g is the band gap (**Fig. 1**). These thermally activated electrons or holes behave like free electrons. In most cases, the mobility of electrons (or holes) is controlled by phonon scattering and decreases with temperature as $\mu_{e,h} \propto \frac{1}{T}$ (Kittel, 1986) (the slight difference between free electrons in metals and electrons and hole non-metallic solids is expressed by the effective mass).

Because the band gap is large for most minerals (several hundreds of kJ/mol) (Nitsan and Shankland, 1976), the contribution from this intrinsic conduction mechanism is small. For instance for Mg_2SiO_4 (forsterite) the electrical conductivity at 1500 K is $\sim 10^{-4}$ S/m (Schock *et al.*, 1989). In comparison, the electrical conductivity of iron-bearing olivine is $\sim 10^{-3}$ S/m for hydrogen-free conditions (Constable *et al.*, 1992), and it is $\sim 10^{-1}$ S/m for hydrogen-rich olivine at the same temperature (Wang *et al.*, 2006). Therefore, the electrical conductivity in typical minerals is usually due to some “impurities” such as ferric iron and hydrogen (**Fig. 2**).

The electrical conductivity in iron-bearing minerals can still be “intrinsic”, i.e., conductivity could occur by the formation of a pair of electrons and holes through reaction (5). However, if this were the dominant mechanism of conduction, then the electrical conductivity would be independent of oxygen fugacity. Laboratory observations on hydrogen-free but iron-bearing minerals often show a positive dependence of electrical conductivity on oxygen fugacity (e.g., (Schock *et al.*, 1989)), showing that the intrinsic conduction is not important in most cases.

In the following we will review two important mechanisms of the electrical conductivity in minerals where impurities play an essential role. When the electrical conductivity is controlled by impurities, the electrical conductivity increases with the

impurity content. However, the relation between the conductivity and impurity content is not always linear. The best-known impurity conduction is the electrical conduction in impurity-doped semi-conductors such as boron-doped Si. In these cases, the charge balance is maintained by the ionization of impurity atoms themselves and if the concentration of impurities is high, electrical conductivity is proportional to \sqrt{N} (N : impurity content) (Kittel, 1986). We will discuss a similar case in hydrogen conduction. In the following we will review the relationship between electrical conductivity and thermo-chemical parameters.

Conductivity due to iron

Outer electrons (in the d-orbit) of Fe (iron) are only weakly bound to the nucleus. Consequently, it is easy to remove an electron from Fe ion to change the valence state from ferrous (Fe^{2+}) to ferric (Fe^{3+}). Ferric iron is an “impurity” in most of minerals where normally ferrous iron occupies the site for doubly charged cation (Mg^{2+}, Fe^{2+}). Consequently ferric iron will produce an impurity level in the band gap to which electrons from the filled valence band can be activated to change ferric iron to ferrous iron (**Fig. 1**). Because this energy level accepts an electron from the valence band, it is sometimes referred to as an “acceptor level”. When this transition occurs by thermal activation, then electric current is carried by (i) hopping of an electron between ferric and ferrous iron or by (ii) the motion of electron hole created in the valence band.

Let us now consider how the presence of such an impurity changes electrical conductivity. In case of iron-bearing minerals, defects such as ferric iron at M-site (Fe_M^\bullet (Kröger-Vink notation)) are formed by the chemical reaction of mineral with the

atmosphere, and the charge balance is maintained by atomic defects, e.g., $[Fe_M^\bullet] = 2[V_M'']$ (V_M'' is the M-site vacancy). This leads to $[Fe_M^\bullet] \propto f_{O_2}^{1/6}$ (somewhat different relationships can be obtained if one assumes different charge neutrality conditions (e.g., (Karato, 1973, Schock *et al.*, 1989)), but conductivity by ferric iron-related species always increases with oxygen fugacity). The electron holes are created from the ferric iron,



where Fe_M^\times denotes Fe^{2+} at M-site and h^\bullet is an electron hole. Applying the law of mass action, one finds that

$$[Fe_M^\bullet] = K_4 [Fe_M^\times] \cdot [h^\bullet] \quad (5)$$

where K_4 is the reaction constant corresponding to the reaction (4) ($K_4 = K_{40} \exp\left(-\frac{H_4^*}{RT}\right)$). In this case, the electrical conduction occurs either by “hopping” of electrons between ferric and ferrous iron or by the conduction by electron hole, and the electrical conductivity may be written as

$$\sigma_{Fe} = |e| [Fe_M^\bullet] \mu_{Fe_M^\bullet} \quad \text{for hopping} \quad (6a)$$

and

$$\sigma_{Fe} = |e| \left[h^{\bullet} \right] \mu_h \quad \text{for free electron hole} \quad (6b)$$

where $\mu_{Fe_M^{\bullet}}$ is the mobility of Fe_M^{\bullet} and μ_h is the mobility of electron hole. (Constable and Roberts, 1997) discussed the mobility of these defects in olivine.

Another well-documented conduction mechanism related to iron is ionic conduction by the diffusion of Mg (or Fe). In addition to the migration of electrons (or holes) just described, ions themselves may carry the electric charge. Because ions have electric charge, they migrate when the electric field is applied. This is called ionic conductivity. The relation between diffusion and electrical conductivity is known as the Nernst-Einstein relation (e.g., (Mott and Gurney, 1940)),

$$\sigma = \frac{f \cdot D \cdot n \cdot q^2}{RT} \quad (7)$$

where n is the concentration of ionic species (per unit volume for a mole), q is the electric charge of that species, D is the diffusion coefficient of the charged species, and f is a non-dimensional constant representing the geometrical factor ($f \sim 1$) (mobility in this case is $\mu = \frac{Dq}{RT}$). Given the concentration and diffusion coefficient of any charged species, one can calculate the electrical conductivity. An obvious mechanism is the electric current carried by the diffusion of constituent ions such as Mg^{2+} (Fe^{2+}). Indeed, several authors suggested that this is an important conduction mechanism in olivine at high temperatures (e.g., (Karato, 1973, Constable, 2006)). These analyses together with the latest results on

diffusion coefficients suggest that the contribution from diffusion of Mg (Fe) is relatively minor compared to the contributions from electronic mechanisms of conduction.

In all cases for iron-related conduction, the electrical conductivity is proportional to the concentration of ferric iron, viz.,

$$\sigma \propto [Fe_M^\bullet]. \quad (8)$$

This relation is different from the well-known relationship for p- or n-type semiconductors (for these materials $\sigma \propto \sqrt{N}$ if impurity concentration is high). The reason is that in iron-bearing minerals, the charge balance is not directly determined by the ionization reaction of iron itself, but it involves chemical reaction with atmosphere (when conduction is due to hydrogen-related defects, the charge balance is sometimes maintained by the ionization reaction. Under these circumstances, one finds $\sigma \propto [H]^r \propto C_w^r$ with $r < 1$ (C_w : water content)).

Since the most important defect for this mechanism is ferric iron whose concentration increases with oxygen fugacity, the electrical conductivity by this mechanism increases with oxygen fugacity. So in general, the electrical conductivity can be written as

$$\sigma_{Fe} \propto f_{O_2}^q \exp\left(-\frac{H_{Fe}^*}{RT}\right) \quad (9)$$

where we used a suffix *Fe* to indicate the quantity is for iron-related mechanism, f_{O_2} is oxygen fugacity, q is the oxygen fugacity exponent ($q > 0$) and H_{Fe}^* is activation enthalpy. The details of this mechanism will be discussed later when we examine the experimental observations.

The electrical conduction by the charge transfer between ferric and ferrous iron (or electron holes created by iron) is often referred to as “(small) polaron” conduction in the geophysical literature (e.g., (Xu *et al.*, 1998b)). The term “polaron” is used to emphasize the fact that the motion of electrons (or holes) in these cases is so slow that moving electrons polarize the surrounding crystal and hence the resistance for electron motion is modified (Yamashita and Kurosawa, 1958) (see also (Bosman and van Daal, 1970)). In other words, the concept of “polaron” was proposed to explain the nature of mobility of electrons. However, the issues of density of charge carrier (its dependence on temperature and chemical environment) are more important in geophysics, and we will not use the term “polaron” (either small or large) in this paper.

(Pearson and Bardeen, 1949) (see also (Debye and Conwell, 1954)) developed a model for impurity conduction where they proposed that the activation energy (enthalpy) for conduction may depend on the impurity concentration, $\sigma \propto N^{1/2} \exp\left[-\frac{H^*}{RT}(1 - \alpha N^{1/3})\right]$ (N : impurity concentration) for high impurity concentration. The idea is that the activation energy for electrical conductivity includes ionization energy that may be affected by the electric field produced by impurities themselves (electric field $\propto N^{1/3}$). However, this effect is weak (it affects the activation energy only when the impurity concentration is ~ 0.1 % or higher), and its effect is present only when the impurity has an effective charge (excess positive or negative

charge compared to the perfect crystal (this is the case for p-, n-type semiconductors)). In most of minerals, the concentration of charged defects is small (the total content of hydrogen can be high, but the majority of hydrogen-related defects is a neutral defect) and this effect will be ignored².

Conduction due to hydrogen

In addition to the electrical conduction due to the diffusion of Mg^{2+} (Fe^{2+}), diffusion of hydrogen may play an important role in the electrical conduction because of the high mobility and potentially large concentration of hydrogen in minerals (Karato, 1990). In the simple model proposed by (Karato, 1990), it was assumed that all the dissolved hydrogen atoms (protons) (in olivine) contribute equally to electrical conductivity, and diffusion coefficient in equation (7) was identified with the chemical diffusion coefficient measured by (Mackwell and Kohlstedt, 1990). In this model, electrical conductivity will be related to the total amount of dissolved water, C_W , water fugacity, f_{H_2O} , and oxygen fugacity, f_{O_2} as

$$\sigma \propto C_W D_W \approx \left[(2H)_M^\times \right] D_W \propto f_{H_2O} f_{O_2}^0 D_W. \quad (10)$$

² Yoshino *et al.* (2008) (see also Yoshino, 2010) argued that the activation energy in minerals containing hydrogen defects depends on the water concentration and applied a formula proposed by Pearson and Bardeen (1949) and Debye and Conwell (1954). However, the use of this model to hydrogen conduction is inappropriate because the dominant hydrogen-bearing defect is neutral relative to the perfect crystal (as discussed later). Yang *et al.* (2011a,b) reached the same conclusion.

where D_W is the diffusion coefficient of hydrogen (water) and we use a model that hydrogen is dissolved in olivine mainly as a neutral defect, $(2H)_M^\times$ (Kohlstedt *et al.*, 1996). In this model, the electrical conductivity increases linearly with water content but independent of oxygen fugacity. Also, the activation energy and anisotropy of electrical conductivity (at a fixed hydrogen content) are the same as those of diffusion.

As we will discuss later, the subsequent studies demonstrated that the dissolution of hydrogen indeed enhances the electrical conductivity in most minerals. However, these studies also showed that some modifications are needed to the initial idea (the activation energy of electrical conductivity is less than that of diffusion, the water content exponent is often less than 1, conductivity is sensitive to oxygen fugacity). An important point is that equation (7) must be generalized where multiple charged species take part in electrical conductivity, i.e.,

$$\sigma = \sum_i \frac{f_i D_i n_i q_i^2}{RT} \quad (11)$$

where a quantity with a suffix i refers to a quantity for the i -th species. Even for a given element such as hydrogen, there are multiple hydrogen-related species in a given material at a given condition as shown by (Nishihara *et al.*, 2008) for wadsleyite. In these cases, the concentration of hydrogen-related species that contributes mostly to conductivity is not necessarily the most abundant hydrogen-bearing species and therefore the electrical conductivity is not necessarily linearly proportional to the total hydrogen (water) concentration.

The addition of hydrogen will also enhance electrical conductivity through the enhancement of diffusion of other species such as Mg (Fe) (Hier-Majumder *et al.*, 2005). Diffusion of Fe (Mg) in olivine or other iron-bearing minerals occurs, in most cases, by the vacancy mechanism, i.e., through the exchange of Fe (Mg) with the M-site (Mg or Fe-site) vacancies, V_M'' . The charge balance in these minerals is dominated by M-site vacancies and ferric iron, $[Fe_M^\bullet] = 2[V_M'']$. In these cases, the electrical conductivity is proportional to ferric iron concentration, and the relation similar to equation (8) or (9) holds (the same oxygen fugacity dependence) although the activation energy for conduction is the same as that for Mg (Fe) diffusion.

Also there is an interaction between ionic and electronic defects in minerals. When charged ionic defects are introduced to a mineral, these defects create electrons or holes. Such a reaction is well known for iron-related defects (reaction (4)). (Wang *et al.*, 2011b) showed that a similar situation will arise for charged hydrogen-related defects. Consequently, ionic and electronic defects need to be considered simultaneously.

These issues will be discussed later when we review experimental and theoretical results.

Electrical conductivity of a multi-phase aggregate

Averaging scheme

Rocks are made of various minerals with different orientations including some fluid phases and grain-boundaries. When different phases have largely different electrical conductivity, then the averaging scheme becomes an important issue. (McLachlan *et al.*, 1990) reviewed such an averaging scheme. In most of practical purposes, the Hashin-

Shtrikman's upper and lower bounds provide good estimates of the electrical conductivity of a mixture. The upper (or lower) bound is given by

$$\sigma_{HS}^{+/-} = \sigma_n + \frac{A^{+/-}}{1 - \frac{A^{+/-}}{3\sigma_n}} \quad (12)$$

with $A^{+/-} = \sum_{i=1}^{n-1} \frac{f_i}{\frac{1}{(\sigma_i - \sigma_n)} + \frac{1}{3\sigma_n}}$ where f_i is the volume fraction of the i -th component, σ_i

is the conductivity of the i -th component, and σ_n is the maximum (or minimum) conductivity (Hashin and Shtrikman, 1962). When we apply the results of electrical conductivity measurements for individual minerals to calculate the electrical conductivity of a rock, we will use these relationships. (Simpson and Tommasi, 2005) discussed the application of such a model to calculate the anisotropy in electrical conductivity in an aggregate with non-random crystallographic orientations.

Influence of element partitioning

In a multi-phase aggregate, various elements are distributed among co-existing minerals. The concentration ratios of these elements are controlled by thermo-chemical equilibrium, and these ratios are referred to as partition coefficients. Particularly important is the partition coefficients of hydrogen. Experimental studies on hydrogen partitioning have been conducted (e.g., (Hauri *et al.*, 2006)) and these results are needed to develop a model of conductivity-depth profile. Because the solubility of an element depends on the physical and chemical conditions, the partition coefficients are dependent on the physical and chemical conditions and not the constants (Karato, 2008a). For

instance, the partition coefficient of hydrogen between olivine and orthopyroxene changes with the total water content (i.e., the water fugacity) by more than a factor of 10 in the upper mantle (Dai and Karato, 2009a). In evaluating the influence of hydrogen partitioning, such an effect needs to be taken into account.

Influence of grain-boundaries

Grain-boundaries are present in any polycrystalline aggregates. Grain-boundaries may enhance or may reduce electrical conduction. When electronic conduction dominates, grain-boundaries act as barriers for the electric current. When ionic conduction plays an important role, grain-boundaries may enhance conduction if grain-boundary diffusion is enhanced. (Roberts and Tyburczy, 1991) and (ten Grotenhuis *et al.*, 2004) studied the influence of grain-size on the electrical conductivity in olivine aggregates. (ten Grotenhuis *et al.*, 2004) found a clear evidence for the contribution of grain-boundary diffusion for their fine-grained synthetic forsterite samples ($\sim 1\text{-}5 \mu\text{m}$). However, a comparison to single crystal data by (Schock *et al.*, 1989) shows that the grain-boundary effect is not important for grain-size larger than $\sim 0.1 \text{ mm}$. Because a typical grain-size in the mantle is several mm (Avé Lallemant *et al.*, 1980), we conclude that the influence of grain-size is not important in most of the Earth's mantle. (Yang and Heidelbach, 2012) also obtained the same conclusion for clinopyroxene.

Influence of fluid phases

Fluids in general have high ionic conductivity and therefore if fluids are present they enhance the electrical conductivity of a rock. Both aqueous fluids (in the crust) and

silicate or carbonatite melts are often invoked to explain high electrical conductivity. The degree to which the presence of fluids affects the electrical conductivity depends on (i) the conductivity ratio of the fluid and mineral, (ii) the volume fraction of the fluid and (iii) the geometry of the fluids (dihedral angle if the fluid geometry is controlled by the interfacial tension).

The influence of partial melt on electrical conductivity was discussed by (Shankland and Waff, 1977), but new experimental observations suggest that some modifications are needed (e.g., (Gaillard *et al.*, 2008, Yoshino *et al.*, 2010)). We will provide a review on the importance of fluids including partial melting incorporating new laboratory and geophysical observations.

Similar to the influence of a fluid phase, the influence of graphite is sometimes proposed (e.g., (Duba and Shankland, 1982)). Graphite has a very high (and anisotropic) conductivity and therefore even a small amount of carbon can enhance conductivity if carbon assumes a connected phase. (Yoshino and Noritake, 2011) studied this issue for the quartz-carbon system and found that carbon does not assume a connected geometry and its influence on electrical conductivity is small. The geometry of carbon in an aggregate is controlled by the interfacial tension and therefore depends on minerals. Similar studies on mantle minerals have not been conducted.

ISSUES ON THE EXPERIMENTAL STUDIES

The measurements of electrical conductivity are relatively simple compared to the measurements of rheological properties (e.g., (Karato, 2008a) and a Chapter by Karato in this book). However, measurements of electrical conductivity in minerals have important

details that need to be discussed to understand the possible causes of different, sometimes conflicting results.

Impedance spectroscopy

Under some conditions, electrical conduction in mineral occurs through the diffusion of ions (ionic conductivity). In these cases, when conductivity is measured using an electrode, moving ions must exchange electrons with an electrode. This requires a finite time, and consequently, finite number of electric charge is accumulated at the electrode forming a capacitor. Similarly, when grain-boundary acts as a barrier for the electric current, then a capacitor will develop at grain-boundaries. In these cases, an equivalent circuit is a parallel combination of a resistor (R) and a capacitor (C), leading to the frequency dependent impedance. The influence of capacitance needs to be corrected by analyzing the whole spectrum of impedance including in-phase (Z') as well as out-of-phase (Z'') response ($Z = Z' - iZ''$, Z : electric impedance, $i = \sqrt{-1}$). Such a method is often called the impedance spectroscopy (Macdonald, 1987) (**Fig. 3**).

For this particular model, Z is given by

$$Z = \frac{R}{1+i\omega RC} \quad (13)$$

where ω is the frequency. In such a measurement, a combination of in-phase and out-phase impedance can be plotted on the $Z' - Z''$ plane (called a Cole-Cole plot (Cole and Cole, 1941)),

$$(Z'(\omega), Z''(\omega)) = \frac{R}{1+\omega^2 R^2 C^2} (1, \omega RC) . \quad (14)$$

For a model of parallel combination of a resistor and a capacitor, the curve $(Z'(\omega), Z''(\omega))$ defines a half circle on the $Z' - Z''$ plane (this can be shown by eliminating ω from equation (14)) (**Fig. 3a**). By fitting the experimental data to this model, one can calculate the resistivity (and hence the conductivity).

In some of the previous studies, only one frequency was used and the resistance was determined by assuming $Z' = R$ (e.g., (Yoshino *et al.*, 2006, Katsura *et al.*, 1998, Yoshino and Katsura, 2009, Yoshino *et al.*, 2008b)). Such a method can be justified only when $\omega RC \ll 1$ because the correct relationship is $Z' = \frac{R}{1+\omega^2 R^2 C^2}$. This inequality is satisfied when both resistance (R) and capacitance (C) are low. This would be the case when temperature is high (low R) and/or when the charge carrier is electron (or electron hole) (low C). Otherwise, the assumption of $Z' = R$ in the one, low frequency measurements leads to a systematic error such as the apparent dependence of activation energy on water content (Karato and Dai, 2009) (this point was also noted by (Yang *et al.*, 2011a, Yang *et al.*, 2011b)).

In some cases, the equivalent circuit may include additional pair of resistor-capacitor combination. This occurs, for instance, when two conduction mechanisms are present in series, say grain-boundary conduction and intra-granular conduction (e.g., (Roberts and Tyburczy, 1991)). In these cases, the $Z' - Z''$ plot contains an additional branch (two half circles, **Fig. 3b**), and the low-frequency data from such an experiments cannot be used if they fall on the second branch.

Another complication is a distorted half circle. In some cases, the half circle is depressed in the Z'' direction (**Fig. 3c**). This occurs when the capacitance shows more complex, distributed behavior so that equation (13) changes to $Z = \frac{R}{1+(i\omega RC)^\alpha}$ ($0 \leq \alpha < 1$; e.g., (Cole and Cole, 1941, Roberts and Tyburczy, 1991, Huebner and Dillenburg, 1995)). Such a behavior was seen, for example, by (Dai and Karato, 2009c, Huebner and Dillenburg, 1995, Reynard *et al.*, 2011). In such a case, although the circle is distorted, the intercepts of a distorted half circle with the Z' -axis are still 0 and R (same as the undistorted half circle). Therefore as far as the dc-resistance is determined by the intercept, one obtains a correct result.

Conductivity measurements of a hydrous sample

Another practical, but important issue, is the fact that when hydrogen-sensitive properties are studied, one needs to pay a great attention to minimize hydrogen loss or gain during an experiment. Hydrogen may be lost during an experiment, but it may also be added to a specimen during an experiment. Therefore in order to obtain reliable results on a sample with some hydrogen (water), the hydrogen (water) content of a sample must be measured both before and after the conductivity measurement, and the change in water content must be small for the results to be accepted. Hydrogen loss during an experiment likely occurs because hydrogen is highly mobile and most of the sample assembly for electrical conductivity measurements is not closed. To minimize the hydrogen loss, one could use relatively low temperatures, but one could also use a lower voltage. However, the use of relatively low temperature creates a problem of extrapolation. In general, activation energy of conduction increases with temperature and in such a case, the

extrapolation from low temperature results tends to underestimate the conductivity at mantle (high) temperatures (**Fig. 4**). In particular, the electrical conductivity at high temperatures due to enhanced diffusion of Mg (Fe) has never been identified by the direct experimental studies of electrical conductivity because all previous studies on the electrical conductivity of hydrous samples were made at relatively low temperatures (to minimize hydrogen loss). The influence of enhanced Mg (Fe) diffusion will be evaluated theoretically based on the experimental results on diffusion in the later section.

Although only hydrogen loss is usually considered, attention should also be drawn to hydrogen addition. A notable example is the case of a study by (Xu *et al.*, 1998b). In that pioneering study, they found that wadsleyite and ringwoodite have much higher electrical conductivity than olivine, and interpreted that wadsleyite and ringwoodite *always* have higher electrical conductivity. (Huang *et al.*, 2005) measured the water contents in the samples studied by (Xu *et al.*, 1998b) and found that these samples of wadsleyite and ringwoodite have a large water content and the higher electrical conductivities of wadsleyite and ringwoodite than olivine is largely due to the higher water contents of wadsleyite and ringwoodite than olivine. In fact, because these minerals have high water solubility, it is difficult to synthesize truly dry wadsleyite and ringwoodite (Nishihara *et al.*, 2006). Truly dry wadsleyite has similar electrical conductivity to dry olivine (Dai and Karato, 2009c, Karato, 2011). Similarly “dry” majorite used by (Yoshino *et al.*, 2008b) contains a large amount (~0.1 wt %) of water. These results should not be interpreted as results for “dry” minerals. (Yoshino *et al.*, 2008a)’s conclusion of “dry mantle transition zone” is based on the use of the data from water-rich samples as “dry” samples and therefore unwarranted.

Also there is an issue on the water content measurements. FTIR (Fourier-Transform Infrared) spectroscopy and SIMS (Secondary Ion Mass Spectroscopy) are most frequently used techniques. For olivine, a significant difference is found between these methods if (Paterson, 1982) calibration is used (Bell *et al.*, 2003). However such a discrepancy does not exist for other minerals investigated (Aubaud *et al.*, 2007). In the following we use the calibration based on SIMS (appropriate corrections have been made on the results from FTIR measurements).

In summary, the critical conditions that need to be met for an experimental study of electrical conductivity are:

- (1) Impedance spectroscopy is used.
- (2) Water content is measured both before and after the conductivity is measured and only a small change in water content during the measurements is documented.
- (3) Water content of a “dry” sample is small (smaller than a few wt ppm for a typical mantle mineral).

In the following, when we analyze the experimental results, we choose the results where all of these conditions are met. In some cases, experimental results that meet all of these conditions are not available. In these cases, we use the available data with some notes on potential problems.

EXPERIMENTAL RESULTS

Table 1 summarizes most of the available experimental results on electrical conductivity of minerals where the influence of water was determined using the

impedance spectroscopy with water content measurements both before and after each experiments. A generic relationship,

$$\sigma = A \cdot \left(\frac{f_{O_2}}{f_{O_2}^0} \right)^q \cdot C_w^r \cdot \exp\left(-\frac{H^*}{RT}\right) \quad (15)$$

is used to interpret the results for each mechanism. This equation contains two parameters characterizing the chemical environment, i.e., f_{O_2} and C_w . This corresponds to the thermodynamic properties of the system that depend on two factors, f_{O_2} and f_{H_2O} (at a fixed oxide activity). Note that the activation enthalpy, H^* , is for a fixed water (hydrogen) content. This choice is made because most of experimental studies are made at a fixed water content, and also the water content in most of Earth's interior is "fixed" (i.e., no diffusional exchange of water (closed system behavior)).

Electrical conductivity for dry (water-free) samples can also be described by this equation by using $r=0$. In a more general case, both hydrogen-independent and hydrogen-dependent mechanisms of conduction operate, and in these cases, contributions from each must be added. For example, when iron-related and hydrogen-related conduction occurs simultaneously, one should use

$$\sigma = A_{Fe} \cdot \left(\frac{f_{O_2}}{f_{O_2}^0} \right)^{q_{Fe}} \cdot \exp\left(-\frac{H_{Fe}^*}{RT}\right) + A_H \cdot \left(\frac{f_{O_2}}{f_{O_2}^0} \right)^{q_H} \cdot C_w^r \cdot \exp\left(-\frac{H_H^*}{RT}\right). \quad (16)$$

In the following, we will review the major observations using selected well-executed experimental results.

Electronic conduction due to iron-related impurities

(Schock *et al.*, 1989) conducted a detailed study of electrical conductivity of iron-bearing, dry (hydrogen-free) olivine where they reported not only the dependence of conductivity on oxygen fugacity but also they measured the Seebeck coefficient to demonstrate that charge carrier has positive charge in iron-bearing, hydrogen-free olivine. Together with point defect analysis (e.g., (Schock and Duba, 1985, Karato, 1973)), these studies showed that the electrical conduction in iron-bearing minerals such as olivine is due mostly to electron holes created by ferric iron, and the conductivity increases with oxygen fugacity as (**Fig. 5**)

$$\sigma_{Fe} = A_{Fe} \cdot \left(\frac{f_{O_2}}{f_{O_2}^0} \right)^{q_{Fe}} \cdot \exp\left(-\frac{H_{Fe}^*}{RT}\right) \quad (17)$$

with q_{Fe} is the oxygen fugacity exponent ($\sim 0.10-0.20$ (Schock *et al.*, 1989, Dai and Karato, 2009c)) and H_{Fe}^* is the activation enthalpy ($\sim 100-150$ kJ/mol). The activation enthalpy depends on either the system is open to the oxidation-reduction reaction or closed. In most of laboratory experiments, the system is open (i.e., equilibrium with the surroundings), whereas in Earth system may be closed (see (Karato, 1973)). However, this effect is relatively small.

Fig. 6 compares electrical conductivity of hydrogen-free samples at $X_{Fe} = \frac{Fe}{Fe+Mg} = 0.1$ for f_{O_2} corresponding to the QFM (quartz-fayalite-magnetite) buffer.

When compared at the same Fe content and oxygen fugacity, electrical conductivity of

different minerals shown here is not much different. This means that the electrical conductivity in iron-bearing minerals is primarily a function of temperature and iron content.

The influence of iron content on the electrical conductivity of (nearly) hydrogen-free olivine was studied by (Cemič *et al.*, 1980). A similar study was conducted on pyrope-almandine garnet by (Romano *et al.*, 2006). These results are summarized in **Fig. 7**. In these studies, the water content of the samples was not measured, but judging from the reported activation energy, we assume that the conduction is mainly due to electron holes created by ferric iron. The influence of iron content may be interpreted in terms of the variation in the pre-exponential term or in the activation energy. If we assume its effect is expressed by the following form,

$$\sigma \propto \exp(\beta X_{Fe}) \quad (18)$$

we get $\beta \approx 9$ for most of minerals where $X_{Fe} = \frac{Fe}{Fe+Mg} (=1-Mg\#/100)^3$ (**Fig. 7**). A similar effect is also found for hydrogen-related conduction. Such a relation can be interpreted by an ionization energy model of activation energy in which the activation energy is inversely proportional to the dielectric constant (the dielectric constant in minerals increases with iron content (Cygan and Lasaga, 1986, Shannon *et al.*, 1991)) (e.g., (Kittel, 1986)) or a model where activation energy is proportional to the melting temperature (melting temperature decreases with iron content). The effect of iron is not

³ $Mg\#=100[Mg/(Mg+Fe)]$ where Mg and Fe are the molar fraction of Mg and Fe respectively.

large in the mantle where the chemical composition is nearly homogeneous. For example, a variation in iron content of 0.02 (i.e., a change in Mg# of 2) results in the change in conductivity of a factor of ~ 20 %. However, the difference in the iron content is large between the crust and mantle ($\Delta X_{Fe} \approx 0.3-0.5$), that results in a factor of ~ 10 or more difference in conductivity.

(Xu *et al.*, 2000) reported results on the experimental studies to determine the pressure effects on electrical conductivity of iron-bearing olivine with little hydrogen (again the water content of the samples was not measured but judging from the reported activation energy, we infer that the conduction is due to electron holes created by ferric iron). They showed a weak pressure effect (conductivity is reduced by pressure, but only by a factor of ~ 2 by a change in pressure of 10 GPa). Expressed in terms of activation volume, $V^* = 0.6 \pm 0.6$ cc/mol. (Dai and Karato, 2009b) reported the pressure effects on conductivity in dry pyrope where conduction is likely due to ferric iron (or electron hole). The observed pressure effect is similarly modest: pressure reduces conductivity by a factor of ~ 10 by 12 GPa. Again in terms of activation volume, the results implies $V^* = 2.5 \pm 0.5$ cc/mol.

Conduction due to hydrogen-related impurities

The possibility of enhanced conduction by proton was first proposed by (Karato, 1990) motivated by the reported high diffusion coefficient of hydrogen (Mackwell and Kohlstedt, 1990). This hypothesis was first examined by (Wang *et al.*, 1999) for diopside. But because natural samples were used in their study, it is not clear if the different conductivity is due to the different hydrogen content or the concentration of some other

impurities. The first definitive test of this model was made by (Huang *et al.*, 2005) for wadsleyite and ringwoodite, and later for olivine (Wang *et al.*, 2006), for pyrope garnet (Dai and Karato, 2009b), for orthopyroxene (Dai and Karato, 2009a, Yang *et al.*, 2011a), and clinopyroxene and plagioclase (Yang *et al.*, 2011a, Yang *et al.*, 2011b). These results show that, when hydrogen content is high (typically higher than $\sim 10^{-3}$ wt% water), electrical conductivity is higher than those values expected from ferric iron-related conduction and the activation energy is smaller, and the conductivity increases with hydrogen (water) content (**Fig. 8**) as

$$\sigma_H = A_H \cdot C_W^r \cdot \left(\frac{f_{O_2}}{f_{O_2}^0} \right)^{q_H} \cdot \exp\left(-\frac{H_H^*}{RT}\right) \quad (19)$$

with $r=0.6-1.0$ and $H_H^*=70-100$ kJ/mol, and in case the oxygen fugacity dependence is determined, it shows a negative correlation, i.e., $q_H < 0$ (Dai and Karato, 2009c).

These studies essentially support the hypothesis of (Karato, 1990) that hydrogen enhances electrical conductivity, but in details, these observations do not agree with some aspects of the simple model by (Karato, 1990). First the activation energy of electrical conductivity due to hydrogen is considerably smaller ($\sim 70-100$ kJ/mol) than the activation energy of hydrogen diffusion (~ 150 kJ/mol) (e.g., (Hae *et al.*, 2006, Kohlstedt and Mackwell, 1998)), second the dependence of electrical conductivity on the water content is not always as expected from the simple model, and third the electrical conductivity in hydrogen-bearing minerals depends on oxygen fugacity although the original model predicts no dependence on oxygen fugacity.

Such deviations from the simple model can be explained by a hybrid model of hydrogen dissolution (Karato, 2006). In this model, we consider that the hydrogen atoms dissolved in minerals are present as several different species and the concentrations of hydrogen with various species is controlled by the thermodynamic equilibrium (and by the charge balance). For example, when a majority of hydrogen atoms goes to the M-site as a neutral defect, $(2H)_M^\times$, that defect can be ionized as



where H'_M is a M-site vacancy that contains one proton (**Fig. 9**) and H^\bullet is “free” proton. In most cases the concentrations of H'_M and H^\bullet are less than that of $(2H)_M^\times$. However if the mobility of H'_M or H^\bullet is larger than that of $(2H)_M^\times$, then contributions from these minority defects can be important. There are a few observations that are consistent with this hybrid model. First, (Nishihara *et al.*, 2008) found that several infrared absorption peaks of wadsleyite correspond to different hydrogen-defects $\left((2H)_M^\times, H'_M, H^\bullet\right)$.

When ionization of a neutral defect occurs as shown by equation (21), then the concentrations of charged defects can be calculated as a function of water fugacity using the law of mass action and appropriate charge balance relationship. It can be shown that the concentration of H^\bullet depends on the water fugacity (and hence the total water content (we use $C_W \propto f_{H_2O}$, for olivine and wadsleyite)) as (Karato, 2006),

$$[H^\bullet] \propto f_{H_2O}^{1/2} f_{O_2}^{-1/12} \quad \text{for} \quad [Fe_M^\bullet] = 2[V_M''] \quad (21a)$$

and

$$[H^\bullet] \propto f_{H_2O}^{3/4} f_{O_2}^{-1/8} \quad \text{for} \quad [Fe_M^\bullet] = [H_M'] \quad (21b)$$

respectively. The experimental observations for of $r < 1$ olivine, wadsleyite and ringwoodite and $q < 0$ (for wadsleyite) are consistent with a model where much of the current is carried by free proton H^\bullet not by a neutral defect $(2H)_M^\times$.

The ratio of concentration of mobile free protons and immobile neutral defects,

$\frac{[H^\bullet]}{[(2H)_M^\times]} \approx \frac{[H^\bullet]}{C_W}$ depends on how deep a hydrogen atoms is trapped at M-site (**Fig. 9**). The

deeper the trap is, the less free protons will be present. Because the depth of the potential where hydrogen is trapped at M-site is related to hydrogen solubility (the deeper the trap,

the larger the solubility), it is expected that wadsleyite has a smaller $\frac{[H^\bullet]}{C_W}$ than olivine.

Consequently, for the same total water content wadsleyite will have lower electrical

conductivity than olivine. Also this model indicates that the majority of hydrogen-related

defect is the neutral defect, $(2H)_M^\times$. The model by (Pearson and Bardeen, 1949, Debye

and Conwell, 1954) is a model for charged impurities. Therefore the application of this

model to hydrogen conduction in minerals proposed by (Yoshino, 2010) is inappropriate.

Also if this model for p- or n-type semiconductor (with high impurity content) were to be

used, then $\sigma \propto C_W^{1/2} \exp\left[-\frac{H^*}{RT}\left(1 - \alpha C_W^{1/3}\right)\right]$ should be used as a concentration dependence

of electrical conductivity (Yoshino's group used $\sigma \propto C_W \exp\left[-\frac{H^*}{RT}\left(1 - \alpha C_W^{1/3}\right)\right]$). (Karato

and Dai, 2009) showed that the concentration dependence claimed by Yoshino's group is an artifact of the experimental technique they used. Also (Yang *et al.*, 2011a, Yang *et al.*, 2011b) found no dependence of activation energy on water content when impedance spectroscopy is used, although they found somewhat higher values of r . In fact our revised calculation for pyrope also shows a similarly larger r ($r \sim 1$; **Table 1**). It appears that minerals where dominant hydrogen-bearing species is $(H \cdot Al)_{Si}^{\times}$ has $r \sim 1$, but minerals where dominant hydrogen-bearing species is $(2H)_M^{\times}$ has a lower value of r . This suggests that the mobility of hydrogen in $(H \cdot Al)_{Si}^{\times}$ is higher than that in $(2H)_M^{\times}$.

Fig. 10 compares the electrical conductivity of hydrogen-bearing minerals including hydrous minerals (for the water content of 0.01 wt%). A comparison is made for $X_{Fe} \approx 0.1$ to minimize the influence of iron content. For hydrous minerals, the conductivities are shown after normalization to 0.01 wt%, i.e., the conductivity of hydrous minerals is normalized by $\sigma_{hyd} \frac{0.01}{C_{w,hyd}}$ where σ_{hyd} is the conductivity of a hydrous mineral and $C_{w,hyd}$ is the water content of the hydrous minerals (in wt%). Because the densities of these minerals are similar ($\sim 3 \pm 0.3$ g/cm³) and the charge of proton is common, a comparison of the conductivity after this normalization is essentially a comparison of the mobility of hydrogen. The results show a systematic trend in normalized conductivity, i.e., hydrogen mobility. Hydrogen mobility in hydrous minerals is lower than that in nominally anhydrous minerals. Among nominally anhydrous minerals, the following trends can also be seen. Nominally anhydrous minerals with high hydrogen solubility (e.g., wadsleyite and ringwoodite) have low hydrogen mobility that is consistent with the previous discussion (see **Fig. 9**). (Schmidbauer *et al.*, 2000) provided

clear evidence that electrical conductivity in (Fe-rich) amphibole is caused by ferric iron rather than proton, a result consistent with our interpretation of low mobility of hydrogen in this mineral. Also, minerals that have $r \sim 1$ tend to have higher mobility than those with $r = 0.6-0.7$. Again this supports the previous discussion that the difference in r may be due to the different hydrogen mobility.

(Hier-Majumder *et al.*, 2005) argued that $(2H)_M^\times$ does not contribute to electrical conductivity because it is a neutral defect. This statement is incorrect. $(2H)_M^\times$ is a neutral defect *relative to the perfect lattice*, but does have electric charge *relative to the vacuum*. Applied electric field exerts a force on each ion in an ionic crystal that has neutral charge relative to the perfect lattice but has electric charge relative to the vacuum. This leads to the well-known phenomena such as dielectric polarization and ionic conduction (see some textbooks of condensed matter physics, e.g., (Mott and Gurney, 1940, Kittel, 1986, Kingery *et al.*, 1976)). The inferred small contribution of $(2H)_M^\times$ is not because it is neutral relative to the perfect crystal but because of its low mobility because hydrogen is strongly trapped in these defects.

Fig. 11 summarizes the influence of iron and hydrogen on the electrical conductivity of typical minerals where electrical conductivity is due either to iron-related or hydrogen-related defects. Both types of defects have important influence on the electrical conductivity, but for a typical mantle where peridotite dominates electrical conduction, the hydrogen effect is more important than the effect of iron because of a narrow range of iron content. However, when we consider regions where both crustal

component (MORB) and the peridotitic component are present (e.g., the D'' layer), then the influence of iron is also important⁴.

The addition of hydrogen will also enhance the electrical conductivity through the enhancement of diffusion of other ions such as Mg and Fe as discussed by (Karato, 1990). (Hier-Majumder *et al.*, 2005) reported such an effect in olivine. If the enhancement of diffusion of Mg (Fe) is due to the increased number of $(2H)_M^\times$ as discussed by (Hier-Majumder *et al.*, 2005), then

$$\sigma_{wet} \propto f_{H_2O}^1 f_{O_2}^0 \propto C_w \cdot \exp\left(-\frac{H_{wet}^*}{RT}\right) \quad (22)$$

where H_{wet}^* is activation enthalpy. Because the activation enthalpy for this mechanism is higher than that of hydrogen diffusion mechanism, this effect is important at high temperatures⁵. However, because most of the measurements on hydrous minerals were conducted at low temperatures, this effect was not detected in the previous experimental studies. The electrical conductivity due to enhanced diffusion of Mg (Fe) can be calculated from the Nernst-Einstein relation, equation (7), and is $\sim 5 \times 10^{-3}$ S/m for the total water content of 10^{-2} wt% at 1600 K. This is about one order of magnitude smaller than the electrical conductivity due to proton ($\sim 3 \times 10^{-2}$ S/m). Therefore the influence of this mechanism is relatively minor in olivine. A similar effect is expected to be present in

⁴ Crustal components (i.e., eclogite) may be present in the main part of the mantle (e.g., Sobolev *et al.*, 2007) but its volume fraction is small and its influence is not important in most of the mantle.

⁵ If the activation enthalpy is defined at fixed water content, then $H_{wet}^* \approx 170$ kJ/mol for this mechanism.

other minerals such as wadsleyite (e.g., (Kubo *et al.*, 2004, Farber *et al.*, 2000)) although no detailed study was made to quantify such an effect for wadsleyite. When these effects are included, the influence of hydrogen on electrical conductivity will be higher than the previous estimates.

The addition of water (proton) also modifies the electronic structure. **Fig. 12** shows the results of calculations of density of states of electrons in forsterite (Mg_2SiO_4 olivine) (Wang *et al.*, 2011b). **Fig. 12a** shows the calculated density of states in forsterite without hydrogen-related defect. **Fig. 12b** shows the density of state of forsterite where only a neutral defect $(2H)_M^\times$ is considered. In this case, the density of states (the band structure) is essentially unchanged from hydrogen-free forsterite. However, when charged defects such as H'_M and H^\bullet are introduced, a new acceptor level is created above the edge of the valence band (**Fig. 12c**). The presence of such an impurity level enhances electrical conductivity exactly in the same way as ferric iron enhances conductivity. (Wang *et al.*, 2011a) showed that the impurity level created by the addition of charged hydrogen-related defect can explain the observed conductivity of hydrous olivine with a reasonable assumption of the mobility of electrons (or holes). We conclude that in addition to the direct contribution to conductivity through the migration of free proton (H^\bullet), dissolution of hydrogen enhances electronic conduction through the creation of an impurity level in the band gap. These two mechanisms may have different conductivity anisotropy.

Dependence of hydrogen-assisted conductivity on iron content has not been determined. However, if we use the results of dependence of hydrogen solubility on iron content (e.g., (Zhao *et al.*, 2004)), then we can predict that the electrical conductivity at a

given water fugacity will increase with iron content due to the increase in hydrogen solubility. In addition, a comparison of the results by (Dai and Karato, 2009a) and (Yang *et al.*, 2011a) on orthopyroxene with the same hydrogen content but different iron content shows that the electrical conductivity of hydrogen-bearing orthopyroxene increases with iron content at the same hydrogen content. This suggests that iron increases the mobility of hydrogen (or electron hole created by hydrogen defect).

Influence of partial melting

Melts in general have higher electrical conductivity than minerals. This is essentially due to the high diffusion coefficients of charged species in melts (e.g., (Hofmann, 1980)). Consequently, the presence of partial melt will contribute to high electrical conductivity.

The importance of partial melt on electrical conductivity depends on (1) the conductivity ratio between the melt and the mineral, (2) the volume fraction of melt and (3) the melt geometry (dihedral angle). (Shankland and Ander, 1983, Shankland and Waff, 1977) analyzed the influence of partial melting on electrical conductivity in the asthenosphere and concluded that a large melt fraction (a few %) is needed to enhance conductivity appreciably. (Gaillard *et al.*, 2008) provided a new data set on carbonatite melt showing high conductivity, and (Yoshino *et al.*, 2010) measured the electrical conductivity of olivine + basaltic, olivine + carbonatite melts with equilibrium melt geometry. These recent studies showed that if more than ~1 % of these melts are present then the conductivity will be enhanced to be $\sim 10^{-1}$ S/m or higher (**Fig. 13**) (a similar result was obtained by (Ni *et al.*, 2011) for a hydrous basaltic melt). Although these

studies showed somewhat larger effect of partial melt than those by (Shankland and Ander, 1983, Shankland and Waff, 1977), $\sim 1\%$ of melt occurs only at the vicinity of mid-ocean ridges (Plank and Langmuir, 1992, Hirschmann, 2010). In the asthenosphere far from mid-ocean ridges the melt fraction is $\sim 10^{-2}\%$ (e.g., (Plank and Langmuir, 1992, Hirschmann, 2010)) and therefore the influence of partial melting is likely not large in the asthenosphere away from the oceanic ridges.

SOME APPLICATIONS

Electrical conductivity and the Earth and planetary interiors

In this section, we will apply experimental results on electrical conductivity and discuss how the electrical conductivity distribution inferred from geophysical studies may be interpreted by the composition and/or temperature in Earth and planetary interiors. Among various parameters, one needs to consider the influence of water, temperature, major element composition, oxygen fugacity and of partial melting.

We will calculate the electrical conductivity in various regions of Earth (and other planets) from laboratory data and a range of temperature, major element chemistry and water distribution. We assume certain compositional models (e.g., pyrolite for the mantle), and calculate the mineralogy and element partitioning for each mineral. We will also assume temperature (pressure) and oxygen fugacity, and calculate electrical conductivity of each mineral, and then calculate the aggregate conductivity using the Hashin-Shtrikman average scheme. The contrasts of conductivity among different

minerals are modest and therefore the difference between the upper and the lower bounds of the Hashin-Shtrikman average is not large (less than 50%)⁶.

Continental mid- and lower crust

Structure and composition of Earth's mid- and lower crust are expected to be laterally heterogeneous (Rudnick and Fountain, 1995, Rudnick *et al.*, 1998). The most important variables that may affect electrical conductivity are (i) the major element composition (and mineralogy), (ii) temperature, (iii) the water content, and (iv) the degree of partial melting.

The rocks in the continental mid- and lower crust have mafic composition, the dominant minerals being orthopyroxene, clinopyroxene, and plagioclase (+ some hydrous minerals). Electrical conductivity in the lower crust mineral depends strongly on minerals (plagioclase has significantly lower conductivity than clino- and orthopyroxene) (Yang *et al.*, 2011a, Yang *et al.*, 2011b). Also the regional variation in temperature is large (~800-1300 K). Consequently, it is difficult to interpret the results of conductivity distribution in the lower crust uniquely. However, the reported conductivities (10^{-4} - 10^{-1} S/m, (Jones, 1992)) can be accounted for by the combination of composition, temperature and water content. In particular, a detailed review by (Yang, 2011) showed that modestly high conductivity of the continental lower crust ($\sim 10^{-3}$ to 10^{-2} S/m) can be explained by high Fe (in pyroxenes) and Na (in plagioclase) content (+ high temperature) in addition to the effects of hydrogen (**Fig. 14**).

⁶ The difference between the upper and the lower bound is large for the lower crust where the contrast in conductivity among co-existing minerals is large (Yang *et al.*, 2011a).

However, high conductivity on the order of 10^{-2} to 10^{-1} S/m observed in certain regions (e.g., Tibet; (Chen *et al.*, 1996)) is not easy to be attributed to the conduction by nominally anhydrous minerals. Recently, (Wang *et al.*, 2012) showed that the dehydration reaction of amphibole enhances electrical conductivity at high temperature ($T > 800$ K) in amphibolites. This enhancement is not due to the production of aqueous fluids but due to the change in the oxidation states of iron. This leads to highly temperature sensitive conductivity, and the high conductivity (10^{-2} to 10^{-1} S/m) can be explained by the modest temperatures (~ 800 - 900 K) without invoking partial melting or the role of aqueous fluids (**Fig. 14**).

The upper mantle and the transition zone

In contrast to the lower crust, the distribution of temperature and major element chemistry in the mantle is rather uniform except for the lithosphere. However, there is some evidence that the mantle is a mixture of peridotite and eclogite (e.g., (Sobolev *et al.*, 2007)). These two components have largely different iron content and hence electrical conductivity. However, the volume fraction of eclogite is small in most regions ($\sim 5\%$ for MORB source regions), so eclogite has little effect on the bulk conductivity, and the variation in electrical conductivity in the mantle reflects the variation in water content more directly. However, in some source regions of ocean island basalts, the eclogite might occupy ~ 10 - 20% (Sobolev *et al.*, 2007) and in these regions the high conductivity of eclogite will have some effects on the bulk conductivity if eclogite bodies are interconnected.

Fig. 15 shows models of electrical conductivity in the Earth's upper mantle and the transition zone assuming the pyrolite composition. The model is not constructed for the lower mantle because there is no experimental data to evaluate the influence of hydrogen on electrical conductivity in lower mantle minerals. In this model, we assumed a typical adiabatic geotherm (+ small changes due to the latent heat release effect). We assume the pyrolite composition (homogeneous composition). Even though the bulk chemistry is assumed to be constant, oxygen fugacity changes with depth due to self-buffering effect. Oxygen fugacity in Earth's upper mantle is controlled by a reaction among skiaigite ($Fe_3^{2+}Fe_2^{3+}Si_3O_{12}$ garnet), olivine and orthopyroxene (in the garnet peridotite) and decreases with depth relative to the commonly used buffering reactions such as QFM (Frost and McCammon, 2008). Consequently, the oxygen fugacity in the upper mantle decreases significantly with depth (relative to QFM buffer). This has an important effect on electrical conductivity: it decreases iron-related conduction but it increases hydrogen-related conduction. Such effects are included in **Fig. 15** (such effects were not considered by (Yoshino, 2010, Baba *et al.*, 2010, Khan and Shankland, 2012) that results in the systematic error of conductivity of ~one order of magnitude). Similarly, the partitioning of key elements such as iron and hydrogen among minerals will change with depth. Particularly important is the depth variation in hydrogen partitioning. We include this effect using the results by (Irifune and Isshiki, 1998, Bolfan-Casanova, 2005, Mookherjee and Karato, 2010, Mierdel and Keppler, 2004).

Because the temperature variation is small and the major element chemistry changes only a narrow range in the mantle, most of the spatial (depth or lateral) variation in electrical conductivity can be attributed to the variation in water (hydrogen) content. In

our model calculation, we leave the water content as a free parameter and explore a range of its value from zero (dry) to nearly saturated values. The composition including the hydrogen content (measured as a total water content) is kept constant with depth. This corresponds to a model of mantle convection without any large chemical fractionation in the mantle.

These results can be compared with geophysically inferred electrical conductivity. **Fig. 16** summarizes the depth and regional variation of electrical conductivity inferred from the analyses of electromagnetic induction (mostly from (Kelbert *et al.*, 2009), see also (Khan *et al.*, 2011); for more details, see a Chapter by Schultz). Inversion of these data is highly non-unique, and in particular, the depth variation in conductivity is only loosely constrained. If one does not assume any abrupt changes in conductivity with depth, then one will obtain a smoothly varying conductivity with depth. In some of the inversions, discontinuities in conductivity are assumed at certain depths motivated by mineral physics observations and the jump in conductivity is estimated.

Although uncertainties are large, some robust conclusions can be obtained about the distribution of electrical conductivity in the Earth's mantle:

- Electrical conductivity in the asthenosphere is $\sim 10^{-2}$ S/m on average, but locally near the top of the asthenosphere conductivity reaches $\sim 10^{-1}$ S/m. Electrical conductivity of the asthenosphere in the western Pacific is unusually low, $\sim 10^{-3}$ S/m.
- Electrical conductivity in the transition zone is generally higher than that in the asthenosphere. On average, it is $\sim 10^{-1}$ S/m, but in the south-central Europe, the conductivity is low $\sim 10^{-2}$ - 10^{-1} S/m, whereas in the eastern Asia, conductivity is high (~ 1 S/m).

The electrical conductivity of the asthenosphere can be explained by a modest amount of water ($\sim 10^{-2}$ wt%) that is consistent with the geochemical inference (e.g., (Dixon *et al.*, 2002, Hirschmann, 2006)) (**Fig. 17**). The influence of hydrogen will be somewhat higher (by ~ 10 -20 %) when the effects of enhanced Mg (Fe) diffusion (Hier-Majumder *et al.*, 2005) are included. There is no need for partial melting to explain this commonly observed conductivity of the asthenosphere. Most of large lateral variation in conductivity is likely due to the lateral variation in the water content. Unusually low electrical conductivity in the western Pacific asthenosphere (Baba *et al.*, 2010) can also be interpreted by a model by (Karato, 2008b) who proposed that the central-western Pacific asthenosphere is depleted with water due to the deep partial melting associated with the Hawaii plume. A high conductivity near the top of the asthenosphere near ridges, $\sim 10^{-1}$ S/m (Baba, 2005), may require partial melting, but in most of the asthenosphere partial melting is not required to explain the inferred electrical conductivity.

In the transition zone, electrical conductivity is generally higher than that of the upper mantle. The electrical conductivity in the transition zone cannot be explained by a dry mantle model. It should be noted that if one assumes constant water content, then there should be a *drop* in the electrical conductivity at 410-km (the conductivity in the transition zone would be smaller than that in the upper mantle) (**Fig. 15**). Therefore the increase in the conductivity at 410-km implies an increase in water content.

The trade-off between water content and temperature for the transition zone is illustrated in **Fig. 18** (a similar trade-off for the upper mantle can be seen in **Fig. 17**). The average conductivity of the transition zone ($\sim 10^{-1}$ S/m) can be explained by ~ 0.1 wt% water and temperature of 1700-1900 K. The transition zone in the south-central Europe

has a significantly lower conductivity that may partly be attributed to the lower water content (as well as the lower temperature). Transition zone in the East Asia has higher conductivity, ~ 1 S/m. The water content of ~ 1 wt% is needed to explain such a high conductivity. The inferred regional variation in the water content is consistent with the tectonic history of these regions: subduction of old and hence cold lithosphere has occurred for more than ~ 400 Myrs in the East Asia that likely brought a large amount of water to the deep mantle (e.g., (Maruyama, 1997, Maruyama and Okamoto, 2007, Maruyama, 1994)). In contrast, subducting slabs around the Europe are generally young and hence these slabs dehydrate soon after they subduct. Consequently not much water is transported to the deep mantle in these regions (Maruyama and Okamoto, 2007). (Iwamori *et al.*, 2010) presented a similar model of global materials circulation based on the analysis of chemical compositions of the MORB (mid-ocean-ridge basalt) and OIB (ocean-island basalt) (see also a Chapter by Iwamori).

The high conductivity in the transition zone may reflect a large amount of eclogite (subducted oceanic crust). In these cases, eclogite must be connected, and the regional variation in conductivity is attributed to the regional variation in the amount and/or the connectivity of subducted oceanic crust.

The inferred large contrast in the electrical conductivity between the upper mantle and the transition zone implies a large contrast in the chemical composition (either the hydrogen content or the eclogite content or both). In either case, if indeed there is a layering in chemical composition, there must be some large-scale material segregation in the middle mantle (at around 410-km). This is due to the fact that without large-scale material segregation, it is impossible to change the chemical composition of a large

region (>100 km) of the mantle because of the slow diffusion. A plausible model is partial melting at ~410-km (e.g., (Bercovici and Karato, 2003, Karato *et al.*, 2006)) for which some support has been provided by seismological observations (Tauzin *et al.*, 2010).

Recently (Khan and Shankland, 2012) used a sophisticated statistical treatment to infer the water content in the upper mantle and the transition zone from geophysically inferred electrical conductivity profiles. They obtained much lower water contents than those by (Karato, 2011) and (Yoshino *et al.*, 2006). For example, the water content of the upper mantle that they inferred is far less than the well-constrained value by the geochemical studies. Their “dry” models predict much higher conductivity than (Karato, 2011), and as a result, most of the observed conductivity in the upper mantle and the transition can be explained by the “dry” model in their analysis. The reason for this difference is unclear. One possibility is the difference in the treatment of the influence of oxygen fugacity. Although the influence of oxygen fugacity is not as large as that of water, oxygen fugacity can change the conductivity by a factor of ~10 in the deep upper mantle and transition zone (Karato, 2011). In the lab measurements, oxygen fugacity is controlled by some solid-state buffers (Ni-NiO etc.). The oxygen fugacity corresponding to these buffers increases exponentially with pressure (e.g., (Karato, 2008a)). In contrast, in the upper mantle, the oxygen fugacity is likely controlled by a different buffer and decreases with depth relative to the solid-state buffers used in the lab studies (Frost and McCammon, 2008). This leads to the different depth dependence of conductivity for “dry” (Fe-based) conductivity and “wet” (hydrogen-based) conductivity because the dependence of electrical conductivity on oxygen fugacity is opposite between Fe-based

conduction and hydrogen-based conduction (see **Fig. 15**). (Khan and Shankland, 2012) did not make corrections for the oxygen fugacity when they applied the lab data to Earth's mantle. The large difference in the inferred water content between (Karato, 2011) and (Khan and Shankland, 2012) is possibly due to the incorrect treatment of the influence of oxygen fugacity by (Khan and Shankland, 2012). Also important is the treatment of hydrogen partitioning. As emphasized by (Dai and Karato, 2009a), the partitioning coefficient is not a constant but depends on the physical (temperature and pressure) and chemical conditions (water fugacity). This is particularly true for hydrogen partitioning between olivine and orthopyroxene (**Fig. 17**). The analysis by (Khan and Shankland, 2012) does not include such a detail that results in a large difference in the inferred total water content.

The lower mantle

Electrical conductivity of the Earth's lower mantle is also inferred from the analysis of electromagnetic induction using relatively low frequencies (e.g., (Olsen, 1999)). Even the regional variation in electrical conductivity of the lower mantle was inferred down to ~1500 km (Kelbert *et al.*, 2009). Also some constraints have been obtained on the electrical conductivity of the D'' layer from the analysis of electromagnetic coupling of the core and mantle (e.g., (Nagao *et al.*, 2003)).

The electrical conductivity in the shallow lower mantle is similar to that of the transition zone. Interpretation of these results in terms of chemical composition is difficult. (Xu and McCammon, 2002, Xu *et al.*, 1998a) showed that the geophysically inferred conductivity is consistent with the lab data with a plausible temperature.

However, the water content in these samples was not measured and it is impossible to discuss the water distribution across the 660-km from the available laboratory data.

(Ohta *et al.*, 2009, Ohta *et al.*, 2010) measured the electrical conductivity down to the D'' conditions and interpreted the inferred conductivity in terms of the major element composition. They found that the subducted MORB has much higher conductivity than pyrolite presumably due to the high iron content, and suggested that the inferred high conductivity in the deep lower mantle may indicate a high volume fraction of subducted MORB. They also noted an effect of spin transition (transition to low spin state reduces the conductivity) to reduce electrical conductivity in the mid-lower mantle (~1500-2500 km) (**Fig. 19**).

(Dobson and Brodholt, 2000) measured the electrical conductivity of (Mg,Fe)O and suggested that electronic conduction by ferric iron is likely important. (Yamazaki and Irifune, 2003) measured the Mg-Fe diffusion coefficients under the lower mantle conditions. They reported diffusion coefficients of $\sim 10^{-12}$ - 10^{-13} m²/s under most of the lower mantle conditions. If the Nernst-Einstein relation is used (equation (7)), these values are translated to the conductivity of $\sim 10^{-2}$ - 10^{-1} S/m, somewhat lower than the conductivity inferred from geophysical studies (e.g., (Olsen, 1999, Kelbert *et al.*, 2009)). If diffusion of Mg (Fe) in (Mg,Fe)O is enhanced by the addition of hydrogen (e.g., (Demouchy *et al.*, 2007); this effect is small at low pressure but this effect should be higher at higher pressures), the influence of hydrogen may also be important in the electrical conductivity in the lower mantle. Similar studies should also be conducted on perovskite, and the influence of hydrogen on the diffusion in (Mg,Fe)O must be determined at higher pressures.

Applications to the Moon and Mars

Because of the absence of the surface oceans, the electrical conductivity distribution in the Moon was well-constrained from the analysis of electromagnetic induction (Sonett *et al.*, 1971, Sonett, 1982, Hood *et al.*, 1982b, Hood *et al.*, 1982a). In these early studies, the distribution of electrical conductivity was interpreted based on the experimental data on electrical conductivity of hydrogen-free (dry) samples (**Fig. 20**). However, the strong influence of hydrogen on electrical conductivity has recently been demonstrated as has been reviewed in this article, and the evidence for a substantial amount of water in the lunar mantle is reported (e.g., (Saal *et al.*, 2008, Greenwood *et al.*, 2011, Hauri *et al.*, 2011)). Consequently, it is important to reinterpret the lunar conductivity profile in terms of temperature and water distribution. Because the pressure conditions in the Moon correspond to the shallow upper mantle in Earth (<4 GPa), the results shown in **Fig. 15** (**Fig. 17**) can be directly applied to the Moon. One difference is that the oxygen fugacity in the Moon is likely much lower than that in Earth (e.g., (Righter and Drake, 1996)) that reduces conductivity by iron but enhances proton conductivity (lunar iron content and major mineralogy are similar to Earth, see e.g., (Ringwood, 1979, Khan *et al.*, 2007)). The temperatures in the lunar interior inferred from the seismological and gravity observations (Khan *et al.*, 2007) (see also (Lambeck and Pullan, 1980)) are considerably lower than those inferred from electrical conductivity by (Hood *et al.*, 1982a, Hood *et al.*, 1982b) using the dry olivine and orthopyroxene data (**Fig. 20**). It is possible that these differences are caused by the presence of water in the deep lunar interior.

Similarly some preliminary studies have been published on the distribution of electrical conductivity in Mars (e.g., (Verhoeven *et al.*, 2005)). Martian mantle corresponds to the upper mantle and the transition zone of Earth, and therefore nearly complete data set on electrical conductivity is available. For Mars, the influence of high iron content needs to be included. Results on orthopyroxene summarized above suggest that high iron content enhances hydrogen-related conductivity as well as iron-related conductivity, but the exact amount of enhanced conductivity is unknown. More important is the influence of hydrogen. However, the influence of water on electrical conductivity was not included in the previous studies. Water content in Martian mantle is controversial (e.g., (Greenwood *et al.*, 2008, Elkins-Tanton, 2008, Guest and Smrekar, 2007, Dreibus and Wänke, 1985, Breuer and Spohn, 2006)). Once the data set on the electrical conductivity in Mars becomes available, a comparison to the experimental data will provide strong constraints on the hydrogen distribution in Mars that will help us understand the evolution of this planet.

SUMMARY AND PERSPECTIVES

In the geophysical literature, high electrical conductivity (and low seismic wave velocities) was often attributed to the presence of some fluids including melts and aqueous fluids (Shankland *et al.*, 1981, Jones, 1992). During the last several years, there have been extensive studies on the electrical conductivity of minerals with the focus on the influence of hydrogen, and a majority of observed high conductivity can be explained by the solid-state mechanisms involving hydrogen. After reviewing key experimental details, we conclude that if results from properly executed experimental studies are used,

the proposal by (Karato, 1990) of hydrogen-enhanced conductivity is now well supported for the lower crust, upper mantle and transition zone minerals. In most of Earth's interior (lower crust, upper mantle and transition zone), electrical conductivity is dominated by hydrogen. However, the original idea by (Karato, 1990) needs to be modified. In many cases, the enhancement of electrical conductivity by hydrogen is not the direct effect of all the dissolved hydrogen. Not all hydrogen atoms in a mineral have high mobility. The mobility of hydrogen is different among various minerals. A hybrid model is needed to explain the experimental results in which the role of minor hydrogen-bearing defects is emphasized. In addition to ionic defects, electronic defects created by hydrogen-related defects may play an important role. Also, dehydration of hydrous minerals (in the mid- or lower crust) enhances conductivity through the change in the oxidation state of iron.

Some differences were noted between the experimental results from Yoshino's group (for a review see (Yoshino, 2010)) and Karato's group ((Karato, 2011) and a summary presented here). Reasons for these differences were discussed in the previous papers (see e.g., (Karato, 2011, Karato and Dai, 2009)) but reiterated in this paper. Most of our conclusions are also supported by the studies by (Yang *et al.*, 2011a, Yang *et al.*, 2011b) who use the impedance spectroscopy and determine the water content through the careful FTIR spectroscopy (their "dry" samples contain very few water <10 ppm wt). The basic features of the results from Yang's group and those from the Karato's group agree well. In addition to the use of inappropriate, single low frequency in many studies by Yoshino's group, the most serious problem in the studies by the Yoshino's group is the poor characterization of water content in their "dry" samples. The main conclusions from their studies such as "hydrous olivine unable to account for conductivity anomaly at the

top of the asthenosphere” (Yoshino *et al.*, 2006) and “dry mantle transition zone inferred from the conductivity of wadsleyite and ringwoodite” (Yoshino *et al.*, 2008a) are the results of these inappropriate methods used in their studies and are not supported by the well-executed experimental studies. Also there is a major difference in the inferred water content from electrical conductivity by (Khan and Shankland, 2012) and (Karato, 2011). (Khan and Shankland, 2012) calculated much higher conductivity of “dry” mantle than (Karato, 2011) (and than (Yoshino *et al.*, 2006) in case of the upper mantle), that leads to the inferred lower hydrogen contents. The water content of the upper mantle inferred by (Khan and Shankland, 2012) is far less than the value inferred by the geochemical method (the water content of the upper mantle inferred by (Karato, 2011, Dai and Karato, 2009a) agrees with the geochemical estimate). The exact cause of this discrepancy is unclear, but (Khan and Shankland, 2012) did not take into account of the influence of oxygen fugacity, and they did not consider the influence of hydrogen partitioning properly that can lead to a systematic difference in the inferred water content.

The major remaining issue is the influence of hydrogen on the electrical conductivity of the lower mantle minerals. The lower mantle occupies the largest portion of the Earth’s mantle, but currently we have no constraints on the water content in this region from electrical conductivity. Because the dominant point defects in the lower mantle minerals are ferric iron and related defects (McCammon, 1997), and because oxygen diffusion is fast in perovskite (Dobson, 2003), it is not clear if hydrogen enhances electrical conductivity in the lower mantle minerals. Experimental and theoretical studies on the influence of hydrogen on the electrical conductivity in lower mantle minerals are critical to understand the water distribution in the whole Earth.

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REFERENCES

- Aubaud, C., Withers, A.C., Hirschmann, M.M., Guan, Y., Leshin, L.A., Mackwell, S.J. & Bell, D.R., 2007. Intercalibration of FTIR and SIMS for hydrogen measurements in glasses and nominally anhydrous minerals, *American Mineralogist*, 92, 811-828.
- Avé Lallemant, H.G., Mercier, J.-C.C. & Carter, N.L., 1980. Rheology of the upper mantle: inference from peridotite xenoliths, *Tectonophysics*, 70, 85-114.
- Baba, K., 2005. Electrical conductivity structure in marine tectonic settings, *Survey of Geophysics*, 26, 701-731.
- Baba, K., Utada, H., Goto, T., Kasaya, T., Shimizu, H. & Tada, N., 2010. Electrical conductivity imaging of the Philippine Sea upper mantle using seafloor magnetotelluric data, *Physics of the Earth and Planetary Interiors*, 183, 44-62.
- Banks, R.J., 1969. Geomagnetic variations and the electrical conductivity of the upper mantle, *Geophysical Journal of Royal Astronomical Society*, 17, 457-487.
- Bell, D.R., Rossman, G.R., Maldener, J., Endisch, D. & Rauch, F., 2003. Hydroxide in olivine: A quantitative determination of the absolute amount and calibration of the IR spectrum, *Journal of Geophysical Research*, 108, 10.1029/2001JB000679.
- Bercovici, D. & Karato, S., 2003. Whole mantle convection and transition-zone water filter, *Nature*, 425, 39-44.
- Bolfan-Casanova, N., 2005. Water in the Earth's mantle, *Mineralogical Magazine*, 69, 229-257.
- Bosman, A.J. & van Daal, H.J., 1970. Small-polaron versus band conduction in some transition-metal oxides, *Advances in Physics*, 19, 1-117.
- Breuer, D. & Spohn, T., 2006. Viscosity of the Martian mantle and its initial temperature: Constraints from crust formation history and the evolution of the magnetic field, *Planetary and Space Science*, 54, 153-169.
- Cemič, L., Will, G. & Hinze, E., 1980. Electrical conductivity measurements on olivines Mg_2SiO_4 - Fe_2SiO_4 under defined thermodynamic conditions, *Physics and Chemistry of Minerals*, 6, 95-107.
- Chen, L., Booker, J.R., Jones, A.G., Wu, N., Unsworth, M.J., Wei, W. & Tan, H., 1996. Electrically conductive crust in southern Tibet from INDEPTH magnetotelluric surveying, *Science*, 274, 1694-1696.
- Cole, K.S. & Cole, R.H., 1941. Dispersion and absorption in dielectrics I. Alternating current characteristics, *Journal of Chemical Physics*, 9, 341-351.
- Constable, S., 2006. SE03: A new model of olivine electrical conductivity, *Geophysical Journal International*, 166, 435-437.
- Constable, S. & Roberts, J.H., 1997. Simultaneous modeling of thermopower and electrical conduction in olivine, *Physics and Chemistry of Minerals*, 24, 319-325.
- Constable, S., Shankland, T.G. & Duba, A., 1992. The electrical conductivity of an isotropic olivine mantle, *Journal of Geophysical Research*, 97, 3397-3404.

- Cygan, R.T. & Lasaga, A.C., 1986. Dielectric and polarization behavior of forsterite at elevated temperatures, *American Mineralogist*, 71, 758-766.
- 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 pyrope-rich garnet at high temperature and pressure, *Physics of the Earth and Planetary Interiors*, 176, 83-88.
- Dai, L. & Karato, S., 2009c. Electrical conductivity of wadsleyite under high pressures and temperatures, *Earth and Planetary Science Letters*, 287, 277-283.
- Debye, P.P. & Conwell, E.M., 1954. Electrical conductivity of N-type germanium, *Physical Review*, 93, 693-706.
- Demouchy, S., Mackwell, S.J. & Kohlstedt, D.L., 2007. Influence of hydrogen on Fe-Mg interdiffusion in (Mg,Fe)O and implications for Earth's lower mantle, *Contributions to Mineralogy and Petrology*, 154, 279-289.
- Dixon, J.E., Leist, L., Langmuir, J. & Schilling, J.G., 2002. Recycled dehydrated lithosphere observed in plume-influenced mid-ocean-ridge basalt, *Nature*, 420, 385-389.
- Dobson, D., 2003. Oxygen ionic conduction in MgSiO₃ perovskite, *Physics of the Earth and Planetary Interior*, 139, 55-64.
- Dobson, D.P. & Brodholt, J.P., 2000. The electrical conductivity of the lower mantle phase magnesiowüstite at high temperatures and pressures, *Journal of Geophysical Research*, 105, 531-538.
- Dreibus, G. & Wänke, H., 1985. Mars: A volatile rich planet, *Meteoritics*, 20, 367-382.
- Duba, A. & Shankland, T.J., 1982. Free carbon and electrical conductivity in the Earth's mantle, *Geophysical Research Letters*, 9, 1271-1274.
- Elkins-Tanton, L.T., 2008. Linked magma ocean solidification and atmospheric growth for Earth and Mars, *Earth and Planetary Science Letters*, 271, 181-191.
- Farber, D.L., Williams, Q. & Ryerson, F.J., 2000. Divalent cation diffusion in Mg₂SiO₄ spinel (ringwoodite), β phase (wadsleyite), and olivine: implications for the electrical conductivity of the mantle, *Journal of Geophysical Research*, 105, 513-529.
- Frost, D.J. & McCammon, C., 2008. The redox state of Earth's mantle, *Annual Review of Earth and Planetary Sciences*, 36, 389-420.
- Gaillard, F., Malki, M., Iacono-Maziano, G., Pichavant, M. & Scaillet, B., 2008. Small amount of carbonatite melts explains high electrical conductivity in the asthenosphere, *Science*, 322, 1363-1365.
- Greenwood, J.P., Itoh, S., Sakamoto, N., Vicenzi, E.P. & Yurimoto, H., 2008. Hydrogen isotope evidence for loss of water from Mars through time, *Geophysical Research Letters*, 35, 10.1029/2007GL032721.
- Greenwood, J.P., Itoh, S., Sakamoto, N., Warren, P., Taylor, L.A. & Yurimoto, H., 2011. Hydrogen isotope ratios in lunar rocks indicate delivery of cometary water to the Moon, *Nature Geoscience*.

- Guest, A. & Smrekar, S.E., 2007. New constraints on the thermal and volatile evolution of Mars, *Physics of the Earth and Planetary Interiors*, 164, 161-176.
- Guo, X., Yoshino, T. & Katayama, I., 2011. Electrical conductivity anisotropy of deformed talc rocks and serpentinites at 3 GPa, *Physics of the Earth and Planetary Interiors*, in press.
- 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.
- Hashin, Z. & Shtrikman, S., 1962. A variational approach to the theory of effective magnetic permeability of multiphase materials, *Journal of Applied Physics*, 33, 3125-3131.
- Hauri, E.H., Gaetani, G.A. & Green, T.H., 2006. Partitioning of water during melting of the Earth's upper mantle at H₂O-undersaturated conditions, *Earth and Planetary Science Letters*, 248, 715-734.
- Hauri, E.H., Weinreich, T., Saal, A.E., Rutherford, M.C. & Van Orman, J.A., 2011. High pre-eruptive water contents preserved in lunar melt inclusions, *Science*, 333, 213-215.
- Hier-Majumder, S., Anderson, I.M. & Kohlstedt, D.L., 2005. Influence of protons on Fe-Mg interdiffusion in olivine, *Journal of Geophysical Research*, 110, 10.1029/2004JB003292.
- Hirschmann, M.M., 2006. Water, melting, and the deep Earth H₂O cycle, *Annual Review of Earth and Planetary Sciences*, 34, 629-653.
- Hirschmann, M.M., 2010. Partial melt in the oceanic low velocity zone, *Physics of the Earth and Planetary Interiors*, 179, 60-71.
- Hofmann, A.W., 1980. Diffusion in natural silicate melts: A critical review. in *Physics of Magmatic Processes*, pp. 385-417, ed. Hargraves, R. B. Princeton University Press, Princeton.
- Hood, L.L., Herbert, F. & Sonett, C.P., 1982a. The deep lunar electrical conductivity profile: Structural and thermal inferences, *Journal of Geophysical Research*, 87, 5311-5326.
- Hood, L.L., Herbert, F. & Sonett, C.P., 1982b. Further efforts to limit lunar internal temperatures from electrical conductivity determinations. in *Proceedings of the Thirteenth Lunar and Planetary Science Conference, Part 1*, pp. A109-A116.
- Huang, X., Xu, Y. & Karato, S., 2005. Water content of the mantle transition zone from the electrical conductivity of wadsleyite and ringwoodite, *Nature*, 434, 746-749.
- Huebner, J.S. & Dillenburg, R.G., 1995. Impedance spectra of hot, dry silicate minerals and rock: Qualitative interpretation of spectra, *American Mineralogist*, 80, 46-64.
- Inoue, T., 1994. Effect of water on melting phase relations and melt composition in the system Mg₂SiO₄-MgSiO₃-H₂O up to 15 GPa, *Physics of Earth and Planetary Interiors*, 85, 237-263.
- Irfune, T. & Isshiki, M., 1998. Iron partitioning in a pyrolite mantle and the nature of the 410-km seismic discontinuity, *Nature*, 392, 702-705.

- Iwamori, H., Albaréde, F. & Nakamura, H., 2010. Global structure of mantle isotopic heterogeneity and its implications for mantle differentiation and convection, *Earth and Planetary Science Letters*, 299, 339-351.
- Jones, A.G., 1992. Electrical properties of the lower continental crust *in Continental Lower Crust*, pp. 81-143, eds. Fountain, D. M., Archulus, R. & Kay, R. W. Elsevier, Amsterdam.
- Karato, S., 1973. Electrical conductivity of rock forming minerals. *in On the electronic states in minerals*, pp. 1-22 The GDP Committee of Japan, Iiyama, Nagano, Japan.
- 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 Earth's Deep Water Cycle*, pp. 113-129, eds. Jacobsen, S. D. & van der Lee, S. American Geophysical Union, Washington DC.
- Karato, S., 2008a. *Deformation of Earth Materials: Introduction to the Rheology of the Solid Earth*, edn, Vol., pp. Pages, Cambridge University Press, Cambridge.
- Karato, S., 2008b. Insights into the nature of plume-asthenosphere interaction from central Pacific geophysical anomalies *Earth and Planetary Science Letters*, 274, 234-240.
- 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., Bercovici, D., Leahy, G., Richard, G. & Jing, Z., 2006. Transition zone water filter model for global material circulation: Where do we stand? *in Earth's Deep Water Cycle*, pp. 289-313, eds. Jacobsen, S. D. & van der Lee, S. American Geophysical Union, Washington DC.
- Karato, S. & 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. & Jung, H., 2003. Effects of pressure on high-temperature dislocation creep in olivine polycrystals, *Philosophical Magazine*, A, 83, 401-414.
- Katsura, T., Sato, K. & Ito, E., 1998. Electrical conductivity of silicate perovskite at lower-mantle conditions, *Nature*, 395, 493-495.
- Kelbert, A., Schultz, A. & Egbert, G., 2009. Global electromagnetic induction constraints on transition-zone water content variations, *Nature*, 460, 1003-1006.
- Khan, A., Connolly, J.A.D., Maclennan, J. & Mosegaard, K., 2007. Joint inversion of seismic and gravity data for lunar composition and thermal state, *Geophysical Journal International*, 168, 243-258.
- Khan, A., Kuvshinov, A. & Semenov, A., 2011. On the heterogeneous electrical conductivity structure of the Earth's mantle with implications for transition zone water content, *Journal of Geophysical Research*, 116, 10.1029/2010JB007458.
- Khan, A. & Shankland, T.J., 2012. A geophysical perspective on mantle water content and melting: Inverting electromagnetic sounding data using laboratory-

- based electrical conductivity profiles, *Earth and Planetary Science Letters*, 317/318, 27-43.
- Kingery, W.D., Bowen, H.K. & Uhlmann, D.R., 1976. *Introduction to Ceramics*, second edition edn, Vol., pp. Pages, John Wiley & Sons, New York.
- Kittel, C., 1986. *Introduction to Solid State Physics*, 6th edition edn, Vol., pp. Pages, John Wiley & Sons, New York.
- Kohlstedt, D.L., Keppler, H. & Rubie, D.C., 1996. Solubility of water in the α , β and γ phases of $(\text{Mg,Fe})_2\text{SiO}_4$, *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 Physikalische Chemie*, 207, 147-162.
- Kubo, T., Shimojuku, A. & Ohtani, E., 2004. Mg-Fe interdiffusion rates in wadsleyite and the diffusivity jump at the 410-km discontinuity, *Physics and Chemistry of Minerals*, 31, 456-464.
- Kushiro, I., Syono, Y. & Akimoto, S., 1968. Melting of a peridotite nodule at high pressures and high water pressures, *Journal of Geophysical Research*, 73, 6023-6029.
- Lambeck, K. & Pullan, S., 1980. Inferences on the lunar temperature from gravity, stress and flow laws, *Physics of the Earth and Planetary Interiors*, 22, 12-28.
- Macdonald, J.R., 1987. *Impedance Spectroscopy*, pp. 346 John Wiley & Sons, New York.
- 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.
- Maruyama, S., 1994. Plume tectonics, *Journal of Geological Society of Japan*, 100, 24-49.
- Maruyama, S., 1997. Pacific-type orogeny revisited: Miyashiro-type orogeny proposed, *The Island Arc*, 6, 91-120.
- Maruyama, S. & Okamoto, K., 2007. Water transportation from the subducting slab into the mantle transition zone, *Gondwana Research*, 11, 148-165.
- McCammon, C., 1997. Perovskite as a possible sink for ferric iron in the lower mantle, *Nature*, 387, 694-696.
- McLachlan, D.S., Blaszkiewicz, M. & Newnham, R.E., 1990. Electrical resistivity of composite, *Journal of the American Ceramic Society*, 73, 2187-2203.
- Mei, S. & Kohlstedt, D.L., 2000. Influence of water on plastic deformation of olivine aggregates, 1. Diffusion creep regime, *Journal of Geophysical Research*, 105, 21457-21469.
- Mierdel, K. & Keppler, H., 2004. The temperature dependence of water solubility in enstatite, *Contributions to Mineralogy and Petrology*, 148, 305-311.
- Mookherjee, M. & Karato, S., 2010. Solubility of water in pyrope-rich garnet at high pressure and temperature, *Geophysical Research Letters*, 37, 10.1029/2009GL041289.
- Mott, N.F. & Gurney, R.W., 1940. *Electronic Processes in Ionic Crystals*, edn, Vol., pp. Pages, Dover, New York.

- Nagao, H., Iyemori, T., Higuchi, T. & Araki, T., 2003. Lower mantle conductivity anomalies estimated from geomagnetic jerks, *Journal of Geophysical Research*, 108, 10.1029/2002JB001786.
- Ni, H., Keppler, H. & Behrens, H., 2011. Electrical conductivity of hydrous basaltic melts: implications for partial melting in the upper mantle, *Contributions to Mineralogy and Petrology*, 162, 637-650.
- Nishihara, Y., Shinmei, T. & Karato, S., 2006. Grain-growth kinetics in wadsleyite: effects of chemical environment, *Physics of Earth and Planetary Interiors*, 154, 30-43.
- Nishihara, Y., Shinmei, T. & Karato, S., 2008. Effects of chemical environments on the hydrogen-defects in wadsleyite, *American Mineralogist*, 93, 831-843.
- Nitsan, U. & Shankland, T.J., 1976. Optical properties and electronic structure of mantle silicates, *Geophysical Journal of the Royal Astronomical Society*, 45, 59-87.
- Ohta, K., Hirose, K., Ichiki, M., Shimizu, K., Sata, N. & Ohishi, Y., 2010. Electrical conductivities of pyrolitic mantle and MORB materials up to the lowermost mantle conditions, *Earth and Planetary Science Letters*, 289, 497-502.
- Ohta, K., Hirose, K., Shimizu, K., Sasa, N. & Ohishi, Y., 2009. The electrical resistance measurements of (Mg,Fe)SiO₃ perovskite at high pressures and implications for electronic spin transition of iron, *Physics of the Earth and Planetary Interiors*, 180, 154-158.
- Olsen, N., 1999. Long-period (30 days - 1 year) electromagnetic sounding and the electrical conductivity of the lower mantle beneath Europe, *Geophysical Journal International*, 138, 179-187.
- Paterson, M.S., 1982. The determination of hydroxyl by infrared absorption in quartz, silicate glass and similar materials, *Bulletin Mineralogie*, 105, 20-29.
- Pearson, G.L. & Bardeen, J., 1949. Electrical conductivity of pure silicon and silicon alloys containing boron and phosphorus, *Physical Review*, 75, 865-883.
- Plank, T. & Langmuir, A.H., 1992. Effects of melting regime on the composition of the oceanic crust, *Journal of Geophysical Research*, 97, 19749-19770.
- Reynard, B., Mibe, K. & Van de Moortèle, B., 2011. Electrical conductivity of the serpentinised mantle and fluid flow in subduction zones, *Earth and Planetary Science Letters*, 307, 387-394.
- Richter, K. & Drake, M.L., 1996. Core formation in Earth's Moon, Mars, and Vesta, *Icarus*, 124, 513-529.
- Rikitake, T., 1966. *Electromagnetism and the Earth's Interior*, edn, Vol., pp. Pages, Elsevier, Amsterdam.
- Ringwood, A.E., 1979. *Origin of the Earth and Moon*, edn, Vol. Springer-Verlag, pp. Pages, Berlin.
- Roberts, J. & Tyburczy, J.A., 1991. Frequency dependent electrical properties of polycrystalline olivine compacts, *Journal of Geophysical Research*, 96, 16205-16222.
- Romano, C., Poe, B.T., Kredie, N. & McCammon, C., 2006. Electrical conductivity of pyrope-almandine garnets up to 19 GPa and 1700°C, *American Mineralogist*, 91, 1371-1377.

- Rudnick, R.L. & Fountain, D.M., 1995. Nature and composition of the continental lower crust: the lower crustal perspective, *Review of Geophysics and Space Physics*, 33, 267-309.
- Rudnick, R.L., McDonough, W.F. & O'Connell, R.J., 1998. Thermal structure, thickness and composition of continental lithosphere, *Chemical Geology*, 145, 395-411.
- Saal, A.E., Hauri, E.H., Lo Cascio, M., Van Orman, J.A., Rutherford, M.C. & Cooper, R.F., 2008. Volatile content of lunar volcanic glasses and the presence of water in the Moon's interior, *Nature*, 454, 192-195.
- Schmidbauer, E., Kunzmann, T., Fehr, T. & Hochleitner, R., 2000. Electrical conductivity and ^{57}Fe Mössbauer spectra of Fe-bearing calcic amphiboles, *Physics and Chemistry of Minerals*, 27, 347-356.
- Schock, R.N. & Duba, A., 1985. Point defects and the mechanisms of electrical conduction in olivine. in *Point Defects in Minerals*, pp. 88-96, ed. Schock, R. N. American Geophysical Union, Washington DC.
- Schock, R.N., Duba, A.G. & Shankland, T.J., 1989. Electrical conduction in olivine, *Journal of Geophysical Research*, 94, 5829-5839.
- Shankland, T.J. & Ander, M.E., 1983. Electrical conductivity, temperatures, and fluids in the lower crust, *Journal of Geophysical Research*, 88, 9475-9484.
- Shankland, T.J., O'Connell, R.J. & Waff, H.S., 1981. Geophysical constraints on partial melt in the upper mantle, *Review of Geophysics and Space Physics*, 19, 394-406.
- Shankland, T.J. & Waff, H.S., 1977. Partial melting and electrical conductivity anomalies in the upper mantle, *Journal of Geophysical Research*, 82, 5409-5417.
- Shannon, R.D., Subramanian, M.A., Hosoya, S. & Rossman, G.R., 1991. Dielectric constants of tephroite, fayalite and olivine and the oxide additivity rule, *Physics and Chemistry of Minerals*, 18, 1-6.
- Simpson, F. & Tommasi, A., 2005. Hydrogen diffusivity and electrical anisotropy of a peridotite mantle, *Geophysical Journal International*, 160, 1092-1102.
- Sobolev, A.V., Hofmann, A.W., Kuzmin, D.V., Yaxley, G.M., Arndt, N.T., Chung, S.-L., Danyushevsky, L.V., Elliot, T., Frey, F.A., Garcia, M.O., Gurenko, A.A., Kamenetsky, V.S., Kerr, A.C., Krivolutsкая, N.A., Matvienkov, V.V., Nikogosian, I.K., Rochell, A., Sigurdsson, I.A., Sushchevskaya, N.M. & Teklay, M., 2007. The amount of recycled crust in sources of mantle-derived melts, *Science*, 316, 412-417.
- Sonett, C.P., 1982. Electromagnetic induction in the Moon, *Review of Geophysics and Space Physics*, 20, 411-455.
- Sonett, C.P., Colburn, D.S., Dyal, P., Smith, B.F., Schubert, G. & Schwartz, K., 1971. Lunar electrical conductivity profile, *Nature*, 230, 359-362.
- Stolper, E.M. & Newman, S., 1994. The role of water in the petrogenesis of Mariana trough magmas, *Earth and Planetary Science Letters*, 121, 293-325.
- Tauzin, B., Debayle, E. & Wittingger, G., 2010. Seismic evidence for a global low-velocity layer within the Earth's upper mantle, *Nature Geoscience*, 3, 718-721.
- ten Grotenhuis, S.M., Drury, M.R., Peach, C.J. & Spiers, C.J., 2004. Electrical properties of fine-grained olivine: evidence for grain-boundary transport, *Journal of Geophysical Research*, 109, 10.1029/2003JB002799.

- Verhoeven, O., Rivoldini, A., Vacher, P., Mocquet, A., Choblet, G., Menvielle, M., Dehant, V., van Hoolst, T., Sleewaegen, J., Barriot, J.-P. & Longnonné, P., 2005. Interior structure of terrestrial planets: Modeling Mars' mantle and its electromagnetic, geodetic, and seismic properties, *Journal of Geophysical Research*, 110, 10.1029/2004JE002271.
- Wang, D., Guo, Y., Yu, Y. & Karato, S., 2012. Electrical conductivity of amphibole-bearing rocks: Influence of dehydration, *Contributions to Mineralogy and Petrology*, in press.
- Wang, D., Karato, S. & Liu, Z., 2011a. Influence of hydrogen on the electronic states in olivine: Implications for electrical conductivity, *Geophysical Research Letters*, submitted.
- Wang, D., Liu, Z.-Y., Li, Y. & Bao-Ping, S., 2011b. Electrical properties of hydrous forsterite derived from first-principle calculations, *Chinese Physics Letters*, 28, 10.1088/0256-1307X/1028/1085/059101.
- Wang, D., Mookherjee, M., Xu, Y. & Karato, S., 2006. The effect of water on the electrical conductivity in olivine, *Nature*, 443, 977-980.
- Wang, Z., Ji, S. & Dresen, G., 1999. Hydrogen-enhanced electrical conductivity of diopside crystals, *Geophysical Research Letters*, 26, 799-802.
- Xu, Y. & McCammon, C., 2002. Evidence for ionic conductivity in lower mantle (Mg,Fe)(Si,Al)O₃ perovskite, *Journal of Geophysical Research*, 107, 10.1029/2001JB000677.
- Xu, Y., McCammon, C. & Poe, B.T., 1998a. Effect of alumina on the electrical conductivity of silicate perovskite, *Science*, 282, 922-924.
- Xu, Y., Poe, B.T., Shankland, T.J. & Rubie, D.C., 1998b. Electrical conductivity of olivine, wadsleyite, and ringwoodite under upper-mantle conditions, *Science*, 280, 1415-1418.
- 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.
- Yamashita, J. & Kurosawa, T., 1958. On electronic conduction in NiO, *Journal of Physics and Chemistry of Solids*, 5, 34-43.
- Yamazaki, D. & Irifune, T., 2003. Fe-Mg interdiffusion in magnesiowüstite up to 35 GPa, *Earth and Planetary Science Letters*, 216, 301-311.
- Yang, X., 2011. Origin of high electrical conductivity in the lower continental crust: A review, *Surveys in Geophysics*.
- Yang, X., Keppler, H., McCammon, C. & Ni, H., 2011a. Electrical conductivity of orthopyroxene and plagioclase in the lower crust, *Contributions to Mineralogy and Petrology*, in press.
- Yang, X., Keppler, H., McCammon, C., Ni, H., Xia, Q.K. & Fan, Q., 2011b. Effect of water on the electrical conductivity of lower crustal clinopyroxene, *Journal of Geophysical Research*, 116, 10.1029/2010JB008010.
- Yang, X.-Z. & Heidelbach, F., 2012. Grain size effect on the electrical conductivity of clinopyroxene, *Contributions to Mineralogy and Petrology*, in press.
- Yoshino, T., 2010. Laboratory electrical conductivity measurement of mantle minerals, *Surveys in Geophysics*, 31, 163-206.

- Yoshino, T. & Katsura, T., 2009. Effect of iron content on electrical conductivity of ringwoodite, with implications for electrical structure in the transition zone, *Physics of the Earth and Planetary Interiors*, 174, 3-9.
- Yoshino, T., Laumonier, M., McIsaac, E. & Katsura, T., 2010. Electrical conductivity of basaltic and carbonatite melt-bearing peridotites at high pressures: Implications for melt distribution and melt fraction in the upper mantle, *Earth and Planetary Science Letters*, 295, 593-602.
- Yoshino, T., Manthilake, G., Matsuzaki, T. & Katsura, T., 2008a. Dry mantle transition zone inferred from the conductivity of wadsleyite and ringwoodite, *Nature*, 451, 326-329.
- 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.
- Yoshino, T., Nishi, M., Matsuzaki, T., Yamazaki, D. & Katsura, T., 2008b. Electrical conductivity of majorite garnet and its implications for electrical structure in the mantle transition zone, *Physics of the Earth and Planetary Interiors*, 170, 193-200.
- Yoshino, T. & Noritake, F., 2011. Unstable graphite films on grain boundaries in crustal rocks, *Earth and Planetary Science Letters*, 306, 186-192.
- Zhao, Y.-H., Ginsberg, S.B. & Kohlstedt, D.L., 2004. Solubility of hydrogen in olivine: dependence on temperature and iron content, *Contributions to Mineralogy and Petrology*, 147, 155-161.
- Zhu, M., Xie, H., Guo, J., Bai, W. & Xu, Z., 2001. Impedance spectroscopy analysis on electrical properties of serpentine at high pressure and high temperature, *Science in China, Ser. D*, 44, 336-345.
- Ziman, J.M., 1960. *Electrons and Phonons*, edn, Vol., pp. Pages, Clarendon Press, Oxford.

Fig. 1 Energy band structure of a typical mineral

E_g is the band gap

There are several impurity states in the band gap that provides extrinsic electronic conduction including ferric iron at M-site, Fe_M^\bullet , vacancy at M-site, V_M'' , and a singly charged hydrogen-related defect at M-site, H_M' .

Fig. 2 A comparison of the results on electrical conductivity measurements on olivine

Results for “pure” Mg_2SiO_4 , San Carlos olivine (without hydrogen), San Carlos olivine with hydrogen (0.01 wt%) are compared (forsterite: (Schock *et al.*, 1989), San Carlos olivine: (Constable, 2006), wet olivine: (Wang *et al.*, 2006)). Results on single crystals are averaged to compare with results for polycrystals.

Fig. 3 The Cole-Cole plot of impedance of a sample + electrode where (Z', Z'') are plotted

- (a) The sample + electrode system is modeled as a parallel combination of a resistor and a capacitor. In order to obtain the resistance, the data for a broad frequency range must be analyzed using a model. If one frequency is chosen (shown by a black dot) and resistivity is determined by this through $Z' = R$, then the inferred resistivity (conductivity) has systematic error because the correction for the capacitance is not made (the correct expression is $Z' = \frac{R}{1+\omega^2 R^2 C^2}$). Such a correction is not important when conduction is due to electrons (or holes) (small

C) but such a correction is important when conduction is due to ionic species such as hydrogen.

(b) A case where two sequential conduction mechanisms are present

In this case, there will be two half circles, and the high-frequency one usually corresponds to the electrical conduction in grain interior.

(c) A case where the capacitance has distributed response

Under some conditions, distributed capacitance can be represented by replacing $i\omega RC$ with $(i\omega RC)^{1-\alpha}$ (Cole and Cole, 1941, Roberts and Tyburczy, 1991, Huebner and Dillenburg, 1995). The element that has $Z = R(i\omega RC)^{-\alpha}$ is often called CPE (constant phase element) because it represents a phase angle between Z' and Z'' that is independent of frequency. The impedance for such a circuit is given by $Z = \frac{R}{1+(i\omega RC)^\alpha}$ ($0 \leq \alpha < 1$). In this case, the half circle is distorted.

However, one can still determine the resistance (1/conductivity) from the intercept with the Z' axis ($Z'=R$ at $\omega = 0$).

Fig. 4 A schematic drawing showing a curvature in the $\log \sigma \Leftrightarrow 1/T$ plot when two independent conduction mechanisms are present

In these cases, extrapolation from the low-temperature regime assuming a linear relation will underestimate the true conductivity at mantle temperatures.

Fig. 5 Electrical conductivity of dry (hydrogen-free) olivine as a function of oxygen fugacity (after (Schock *et al.*, 1989))

Electrical conductivity in iron-bearing olivine increases with oxygen fugacity, whereas electrical conductivity of “pure” forsterite (Mg_2SiO_4) shows a more complex oxygen fugacity dependence. Results at 0.1 MPa and $T=1473$ K.

Fig. 6 A comparison of electrical conductivities in various dry (hydrogen-free) samples at $\text{Fe}/(\text{Fe}+\text{Mg})=0.1$ at $f\text{O}_2 \sim \text{QFM}$

Data source: olivine (Constable *et al.*, 1992), pyrope garnet (Dai and Karato, 2009b)

Fig. 7 Dependence of electrical conductivity in hydrogen-free samples on iron content (olivine: (Cemič *et al.*, 1980), pyrope garnet: (Romano *et al.*, 2006), ringwoodite (Yoshino and Katsura, 2009)) (note: for pyrope and olivine, hydrogen content was not measured but based on the activation energy, we infer that the conduction is due to iron-related defects), orthopyroxene (Dai and Karato, 2009a), wadsleyite (Dai and Karato, 2009c)

Fig. 8 (a) Influence of water content on the electrical conductivity of wadsleyite, (b) influence of oxygen fugacity on the electrical conductivity of hydrogen-rich and hydrogen-poor wadsleyite (after (Dai and Karato, 2009c)) (results at $P=15$ GPa)

Fig. 9 A model of hydrogen-related defects in a nominally anhydrous mineral

(a) A majority of hydrogen-related defects in mantle minerals is a neutral defect such as $(2H)_M^\times$ (two protons at M-site vacancy). However, some fraction of these neutral defects are ionized to form charged defects by a reaction

$(2H)_M^\times \Leftrightarrow H'_M + H^\bullet$ (H'_M : one hydrogen trapped at M-site vacancy, H^\bullet : “free” proton)

(b) The energy levels of hydrogen-related defects

At equilibrium the concentrations of these charged defects are controlled by the thermo-chemical equilibrium of the above reaction as well as the conditions of charge balance. The presence of these three defects was inferred for wadsleyite (Nishihara *et al.*, 2008). Even if the concentrations of these defects are smaller than that of a neutral defect, the minority charged defects could control electrical conductivity if the product of mobility and concentration is high. $\Delta E_{1,2}$ is the energy difference between different defects relative to the neutral defect $(2H)_M^\times$.

Fig. 10 Electrical conductivity of hydrogen-bearing minerals normalized to 0.01 wt% of water (thin solid lines are nominally anhydrous minerals with $r \sim 0.6-0.7$, broken lines are nominally anhydrous minerals with $r \sim 1$ and thick solid lines are hydrous minerals (results for hydrous minerals are under the conditions where they are stable. When dehydration occurs, conductivity will change (see **Fig.14**)) (data from samples with $X_{Fe} \sim 0.1$ are chosen (when the iron content is different from $X_{Fe} \sim 0.1$, corrections are made using the relation (18))

When normalized, conductivity of hydrous minerals is generally lower than that in nominally anhydrous minerals showing that the mobility of hydrogen in hydrous minerals is less than that in nominally anhydrous minerals. In these minerals, electrical conduction likely occurs by some other impurities such as

iron-related mechanisms (therefore their conductivity varies largely among different minerals). Also the normalized conductivity of minerals with $r \sim 1$ is generally higher than that of minerals with $r \sim 0.6-0.7$.

Data are from **Table 1** for nominally anhydrous minerals and for hydrous minerals data are from (Reynard *et al.*, 2011, Zhu *et al.*, 2001, Schmidbauer *et al.*, 2000). Modest anisotropy is reported for talc (Guo *et al.*, 2011). We used the average values.

Fig. 11 The influence of hydrogen and iron content on the electrical conductivity of minerals

$$\text{A functional relationship } \frac{\sigma}{\sigma_o} = \left(\frac{C_w}{C_w^o} \right)^r \exp \left[\beta (X_{Fe} - X_{Fe}^o) \right] = \left(\frac{C_w}{C_w^o} \right)^r \exp(\beta \cdot \Delta X_{Fe})$$

is assumed where $C_w^o = 10^{-2}$ wt%, $\Delta X_{Fe} = X_{Fe} - X_{Fe}^o$ ($X_{Fe}^o = 0.1$) and $\sigma_o = 10^{-2}$ S/m ($r=0.7$, $\beta=9$). For the peridotite, the range of X_{Fe} is narrow (± 0.05) and the influence of ΔX_{Fe} is small compared to the influence of C_w / C_w^o , whereas the contrast in X_{Fe} is large between the crust and the mantle ($\Delta X_{Fe} = 0.3-0.5$) and the influence of iron content is large and comparable to the influence of hydrogen. The numbers in the figure show $\log_{10} \frac{\sigma}{\sigma_o}$.

Fig. 12 Influence of the addition of hydrogen on the density of state (DoS) of electrons in forsterite (from (Wang *et al.*, 2011b))

(a) density of state of pure forsterite

(b) density of state of forsterite with a neutral defect, $(2H)_M^\times$

Energy band structure is essentially identical to an impurity-free olivine.

(c) density of state of forsterite with charged defects, H'_M and H^\bullet

An impurity level is created in the band gap close to the edge of the valence band (an acceptor level) similar to the case of ferric iron-bearing olivine.

Electrons occupy various states from the lowest energy level to the maximum level that is determined by the total number of electrons. The maximum energy is defined to be zero energy ($E=0$ eV). Therefore, at the ground state, all electrons belong to the fully occupied energy bands and they are immobile. Electrical conduction occurs only when some electrons are moved to a higher energy level by thermal activation. Such activation is facilitated when an impurity level is created in the band gap.

Fig. 13 Influence of partial melting on the electrical conductivity of upper mantle rocks (Yoshino *et al.*, 2010)

Fig. 14 Electrical conductivity in the lower crust: a comparison of laboratory data with geophysical inference (from (Wang *et al.*, 2012))

Hatched regions correspond to a range of conductivity of the continental lower crust inferred from geophysical studies. This lines with “hydrous” corresponds to minerals containing ~0.04 wt% water, “Dry” correspond to water-free samples. $HS^{+,-}$ correspond to the Hashin-Shtrikman upper and lower bounds respectively. Thick lines are

for amphibolites. Above ~ 800 K, conductivity of amphibolite increases strongly with temperature due to oxidation of iron caused by dehydration.

Fig. 15 Electrical conductivity-depth profiles in Earth's upper mantle and transition zone (from (Karato, 2011)) for various fixed water (hydrogen) content

(a) The assumed geotherm. (b) The calculated conductivity-depth profiles.

The depth variation in the oxygen fugacity is included in the calculation based on the model by (Frost and McCammon, 2008). Water content is assumed to be constant with depth.

Thick broken lines in the transition zone are the results by (Yoshino, 2010) based on the incorrect method of conductivity measurements (see text for details) and their "dry" samples contain ~ 0.01 - 0.1 wt% of water.

Fig. 16 Electrical conductivity-depth profiles for the Earth's upper mantle and transition zone determined from the analysis of electromagnetic induction (after (Karato, 2011))

The thick lines show "average" conductivity and the grey regions show the range of conductivity in various regions.

Fig. 17 (a) The partition coefficient of water (hydrogen) between olivine and orthopyroxene (Dai and Karato, 2009a) (b) The influence of water content and temperature on the electrical conductivity of the asthenosphere (from (Dai and Karato, 2009a))

For the plausible temperature (~ 1600 K), the water content of $\sim 10^{-2}$ wt% is consistent with most of the geophysical observations on the asthenosphere (with some regional variations). The enhanced Mg (Fe) diffusion (Hier-Majumder *et al.*, 2005) will increase the influence of water but its effect is small ($\sim 10\%$) (see text).

Fig. 18 The trade-off between water effect and temperature effect on the electrical conductivity of the upper transition zone

Both iron-related conduction and hydrogen-related conduction are considered. A mixture of 60 % wadsleyite and 40% majorite is assumed. The hatched regions show typical temperature and conductivity values in the upper transition zone. For a conductivity of $\sim 10^{-1}$ S/m (see **Fig. 16**), the water content of ~ 0.1 wt% is inferred.

Fig. 19 Electrical conductivity-depth profiles in the lower mantle (Ohta *et al.*, 2010)

The low conductivity in the middle lower mantle is due to low-spin state of perovskite (and (Mg,Fe)O). Conductivity of MORB is generally higher than that of pyrolite.

Fig. 20 (a) Electrical conductivity profile of the Moon inferred from the observed electromagnetic induction and (b) its interpretation in terms of temperature (from (Hood *et al.*, 1982b))

The temperature-depth model shown here is based on the electrical conductivity of dry (water-free) olivine and orthopyroxene. If the influence of water is included, the inferred temperature will be reduced. A grey region shows the temperature-depth profile

inferred from seismic wave velocities and gravity data by (Khan *et al.*, 2007) ((Lambeck and Pullan, 1980) obtained similar results from the analysis of the gravity anomalies).

Table 1 Electrical conductivity of some representative mineralsNumbers in the parenthesis is an error in the last digit (with one standard deviation) (e.g., 0.90 (4) means 0.90 ± 0.04).

	Mineral	P (GPa)	T (K)	r	α	$\log_{10} A$ (S/m)****	H* (kJ/mol)	Remarks	ref.
Lower crust	orthopyroxene	0.6-1.2	573-1273	-		2.39 (18)	105(3)	Dry, Mg#=67, NNO	(1)
				0.90 (4)		3.83 (10)	81 (1)	Wet, Mg#=67, NNO	
	plagioclase	0.6-1.2	573-1273	-		4.12 (34)	161 (6)	Dry, NNO	(1)
			0.83 (6)		2.49 (14)	77 (2)	Wet, NNO		
	clinopyroxene	1.2	773-1273	-		2.16 (27)	102(5)	Dry, En:F _s :W _o =44:6:50, NNO	(2)
		0.6-1.2	573-1273	1.13 (5)		3.56 (10)	71 (1)	Wet, En:F _s :W _o =44:6:50, NNO	
Upper mantle	olivine	10 ⁻⁴	995-1775			2.40 (10)	154 (4)	Dry, Mg#=90, fo ₂ =10 ⁻⁴ Pa	(3)
	olivine	4	873-1273	0.62 (15)		3.00 (40) ^{a)} 2.70 (40) ^{b)}	87 (5)	Wet, Mg#=90, NNO	(4)
	olivine*	10	500-1000	-	0.16 (2)	1.90 (44) ^{a)}	88 (4)	Wet, Mg#=90, MMO	(5)
	orthopyroxene**	8	873-1473	-		2.73 (1)	147 (6)	[001], dry, Mg#=82, MMO	(6)
				-		2.26 (3)	80 (2)	[001], wet, Mg#=86, MMO	
		8	873-1273	-		2.21 (4)	82 (3)	[100], wet, Mg#=86, MMO	
		-		2.18 (3)	85 (2)	[010], wet, Mg#=86, MMO			
pyrope	8	873-1473	-		3.02 (20)	128 (6)	Dry, Py:Alm:Grs=73:14:13, MMO	(7)***	
		873-1273	1.09 (5)		3.29 (17)	68 (3)	Wet, Py:Alm:Grs=73:14:13 MMO		
Transition zone	ringwoodite	14-16	773-1273	0.69 (3)		3.61 (10)	104 (2)	Wet, Mg#=90, MMO	(8)
	wadsleyite	15	873-1673	-		2.10 (10)	147 (3)	Dry, Mg#=90, MMO	(9)***
873-1273			0.70 (3)		2.57 (16)	90 (3)	Wet, Mg#=90, MMO		

Note: NNO is the Ni-NiO buffer, MMO is the Mo-MoO₂ buffer. Electrical conductivity under “wet” and “dry” condition is expressed by the following relationship,

$$\sigma_w = A \cdot \left(\frac{f_{O_2}}{f_{O_2}^o} \right)^{q_w} \cdot C_w^r \cdot \exp\left(-\frac{H^*}{RT}\right) \quad (\text{wet}), \quad \sigma_d = A \cdot \left(\frac{f_{O_2}}{f_{O_2}^o} \right)^{q_d} \cdot \exp\left(-\frac{H^*}{RT}\right) \quad (\text{dry})$$

respectively where A and r are constants, f_{O_2} is oxygen fugacity, $f_{O_2}^o$ is the reference oxygen fugacity (such as NNO that is shown in the “remarks” in the Table), C_w is the water content in wt %, H^* is activation enthalpy, R is the gas constant and T is temperature. When these results are to be applied to other oxygen fugacity conditions, a correction needs to be made using the above formula. The oxygen fugacity exponent, q , was determined for some minerals. $q_d=0.17$ for dry conditions and $q_w=-0.1$ for wet conditions.

The correction for pressure effect is not large in most cases (because conductivity was measured near the relevant pressure in most cases).

* Yoshino et al. (2009) used $\sigma = A \cdot C_w \cdot \exp\left(-\frac{H^* - \alpha C_w^{1/3}}{RT}\right)$, which is not an appropriate formula as discussed in the text.

** The sample has 0.042 wt% water. The electrical conductivity for wet opx is fitted to $\sigma = A \cdot \exp\left(-\frac{H^*}{RT}\right)$.

***: Data are re-analyzed.

****: The values of A for wet samples of olivine depend on the water content measurement for which different calibrations for FT-IR measurement give a factor of ~3 difference in water content. Such a difference does not exist (or is not known) for other minerals listed here.

a): for Paterson (1982) calibration for water

b): for Bell et al. (2003) calibration of water

(1): (Yang *et al.*, 2011a)

(2): (Yang *et al.*, 2011b)

(3): (Constable *et al.*, 1992)

(4): (Wang *et al.*, 2006)

(5): (Yoshino *et al.*, 2009)

(6): (Dai and Karato, 2009a)

(7): (Dai and Karato, 2009b)

(8): (Huang *et al.*, 2005)

(9): (Dai and Karato, 2009c)

Data source

- Constable, S., Shankland, T.G. & Duba, A., 1992. The electrical conductivity of an isotropic olivine mantle, *Journal of Geophysical Research*, 97, 3397-3404.
- 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 pyrope-rich garnet at high temperature and pressure, *Physics of the Earth and Planetary Interiors*, 176, 83-88.
- Dai, L. & Karato, S., 2009c. Electrical conductivity of wadsleyite under high pressures and temperatures, *Earth and Planetary Science Letters*, 287, 277-283.
- Huang, X., Xu, Y. & Karato, S., 2005. Water content of the mantle transition zone from the electrical conductivity of wadsleyite and ringwoodite, *Nature*, 434, 746-749.
- Wang, D., Mookherjee, M., Xu, Y. & Karato, S., 2006. The effect of water on the electrical conductivity in olivine, *Nature*, 443, 977-980.
- Yang, X., Keppler, H., McCammon, C. & Ni, H., 2011a. Electrical conductivity of orthopyroxene and plagioclase in the lower crust, *Contributions to Mineralogy and Petrology*, in press.
- Yang, X., Keppler, H., McCammon, C., Ni, H., Xia, Q.K. & Fan, Q., 2011b. Effect of water on the electrical conductivity of lower crustal clinopyroxene, *Journal of Geophysical Research*, 116, 10.1029/2010JB008010.
- 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.

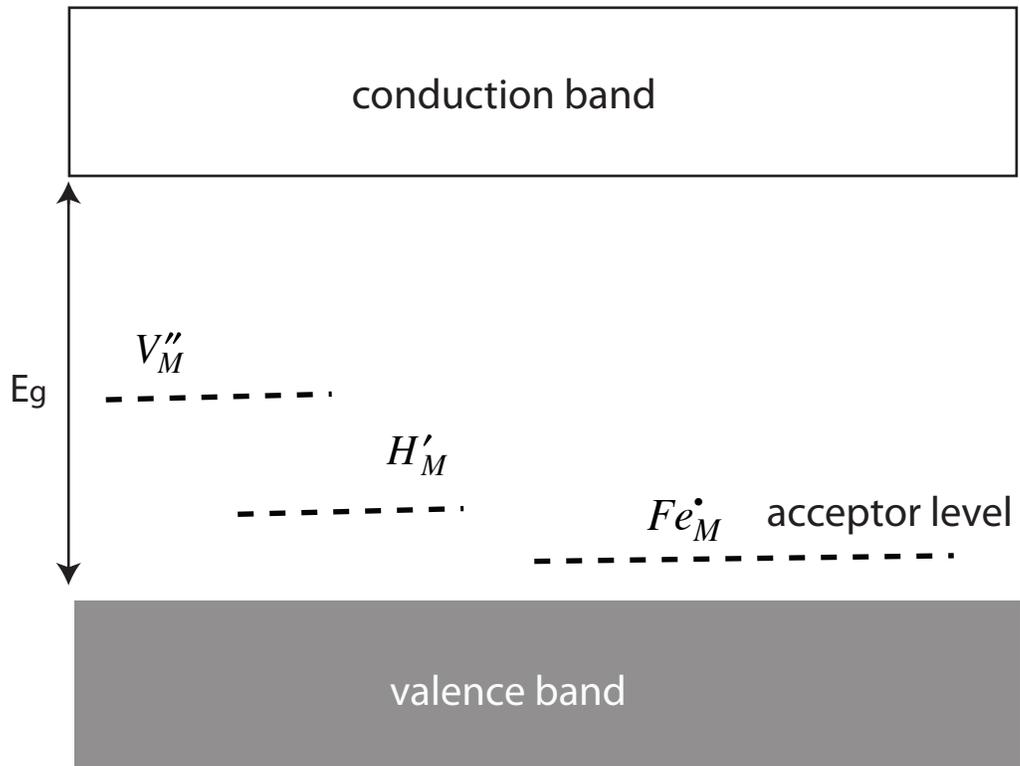


Fig.1 (Karato, II)

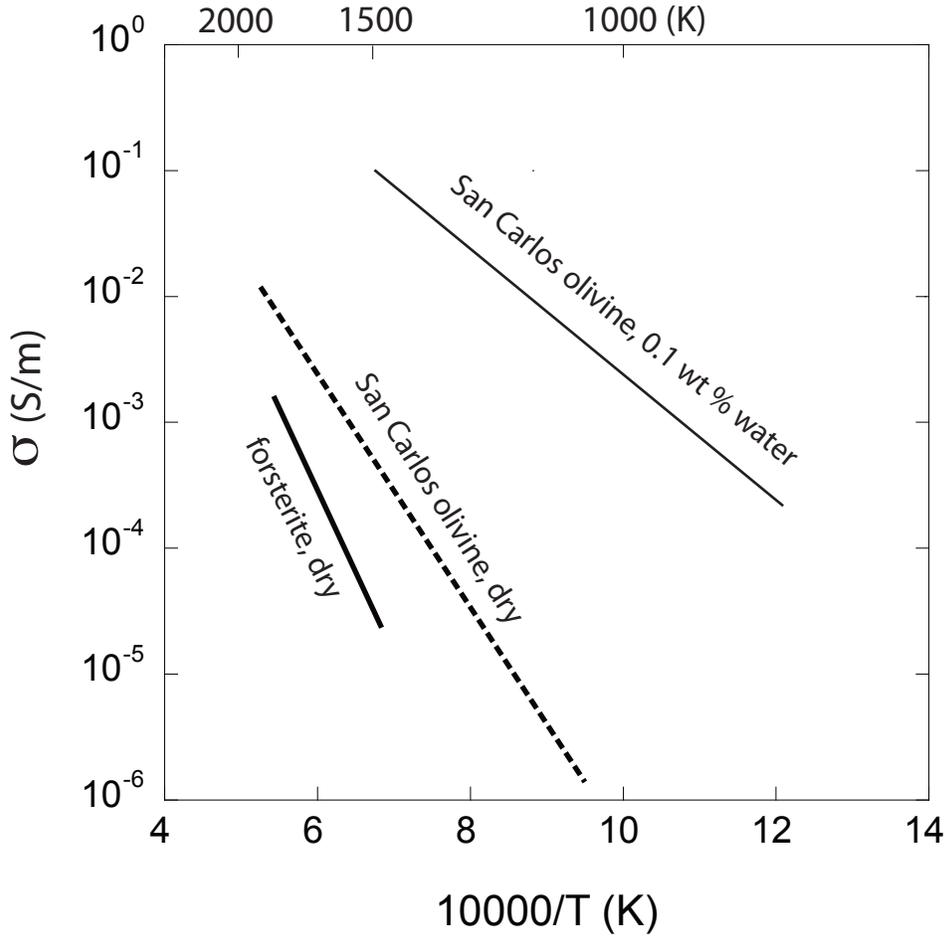
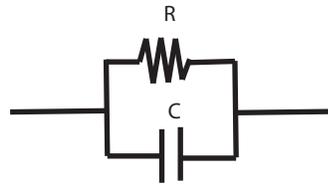
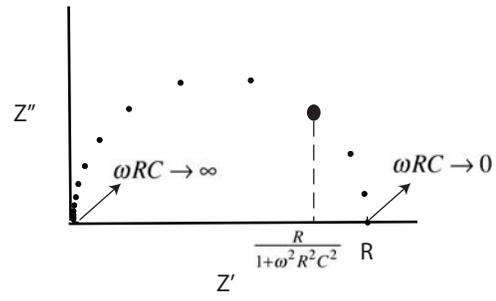
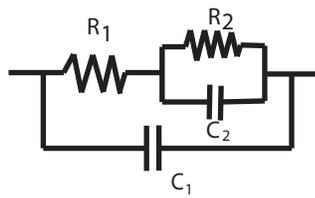
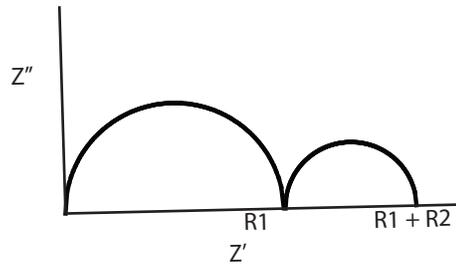


Fig. 2 (Karato-II)

(a)



(b)



(c)

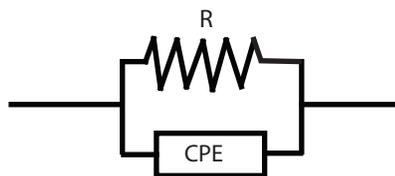
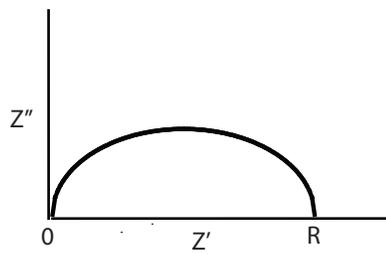


Fig. 3 (Karato-II)

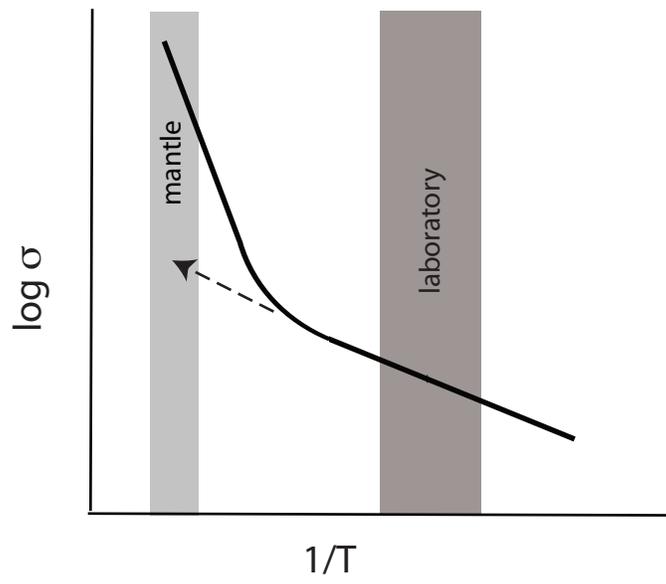
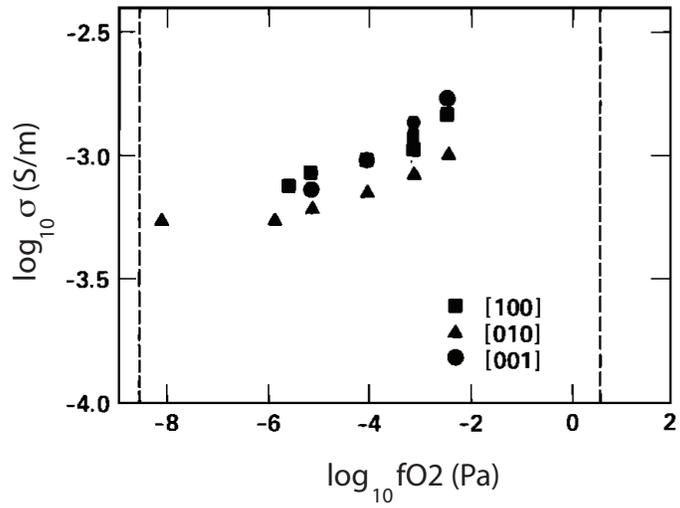


Fig.4 (Karato-II)

(a) San Carlos olivine (iron-bearing olivine)



(b) synthetic Mg_2SiO_4

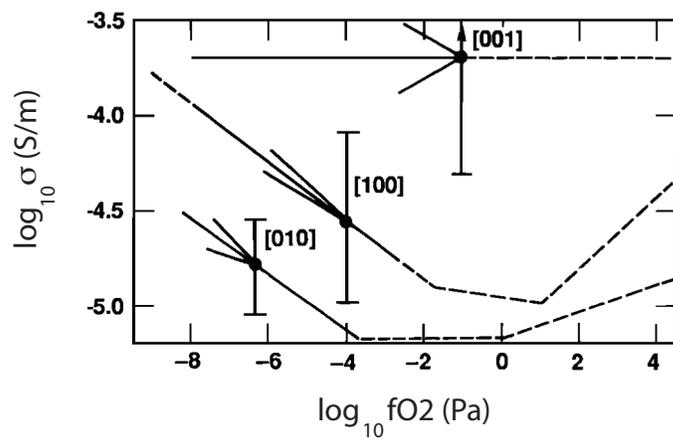
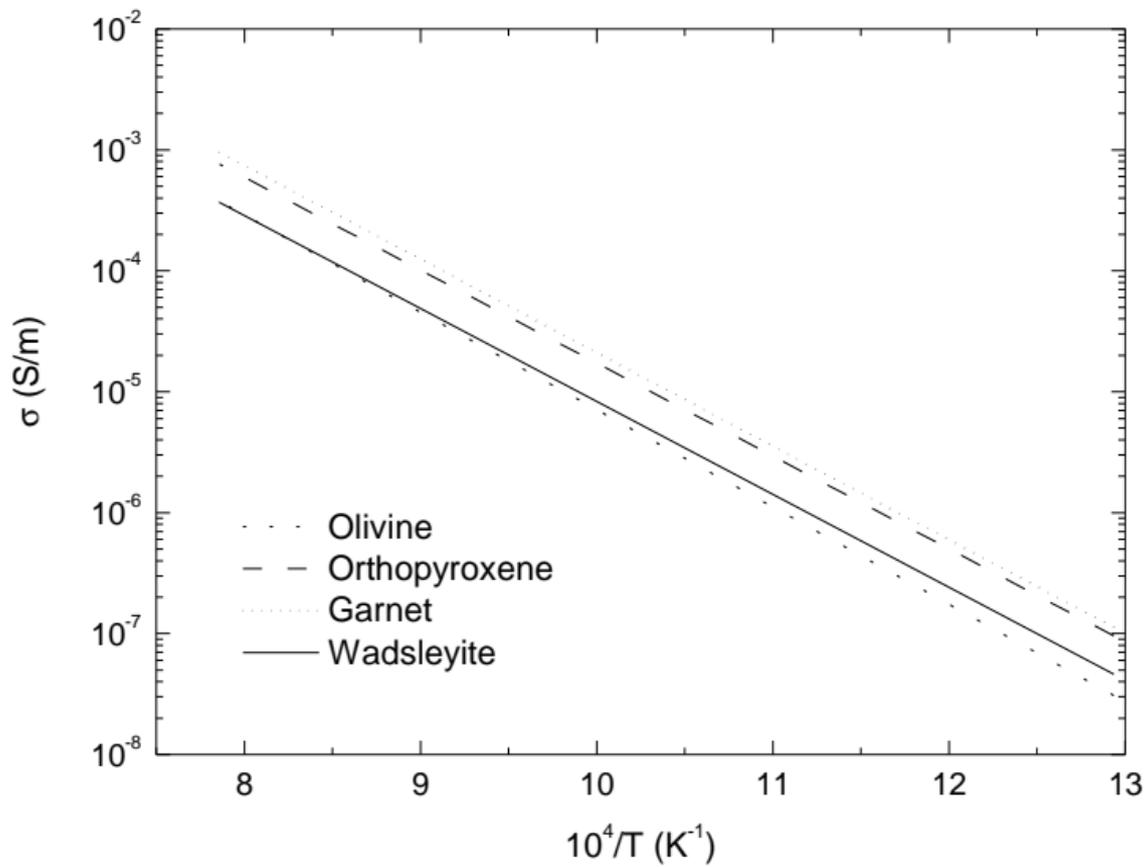
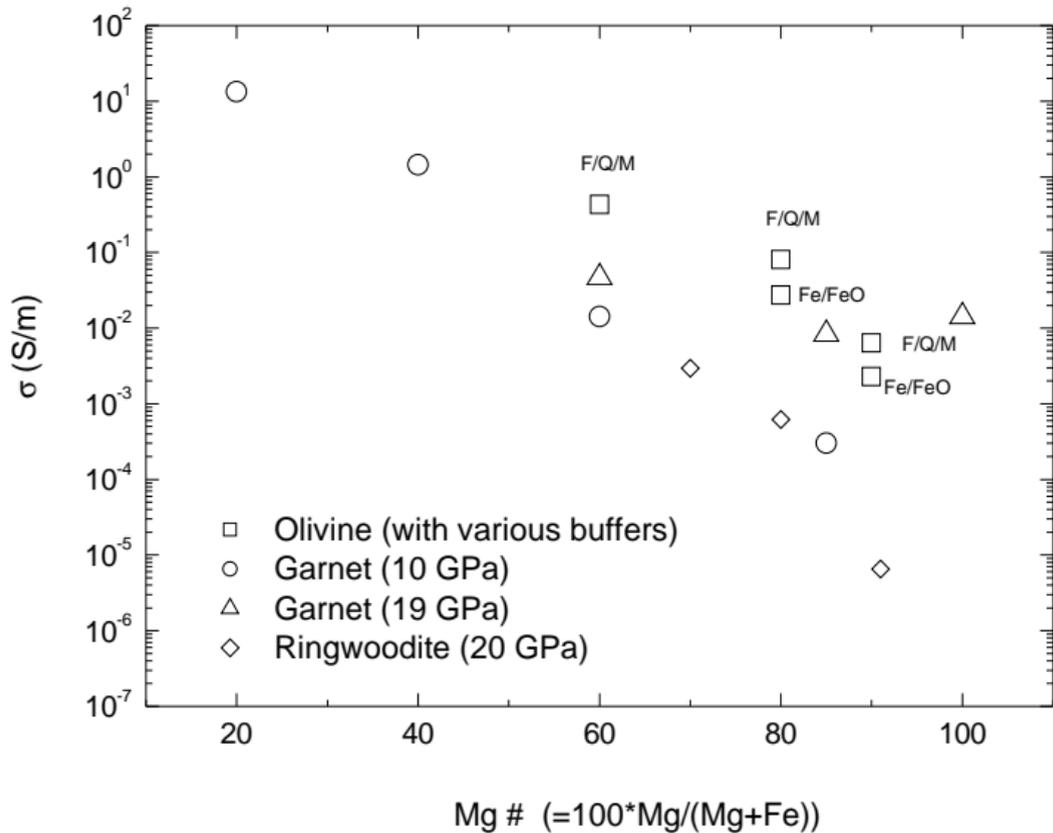
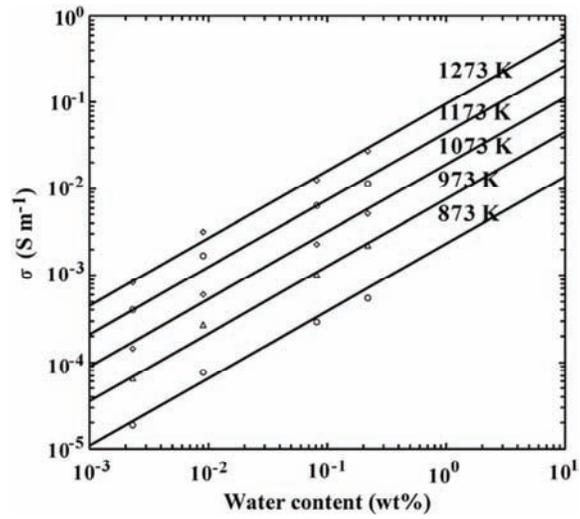


Fig. 5 (Karato-II)





(a) water content dependence



(b) oxygen fugacity dependence

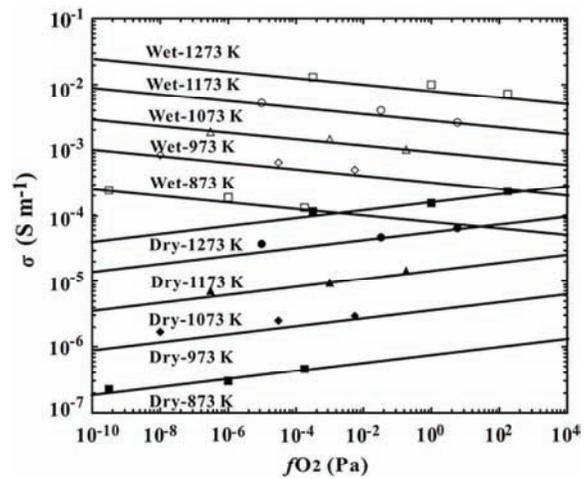
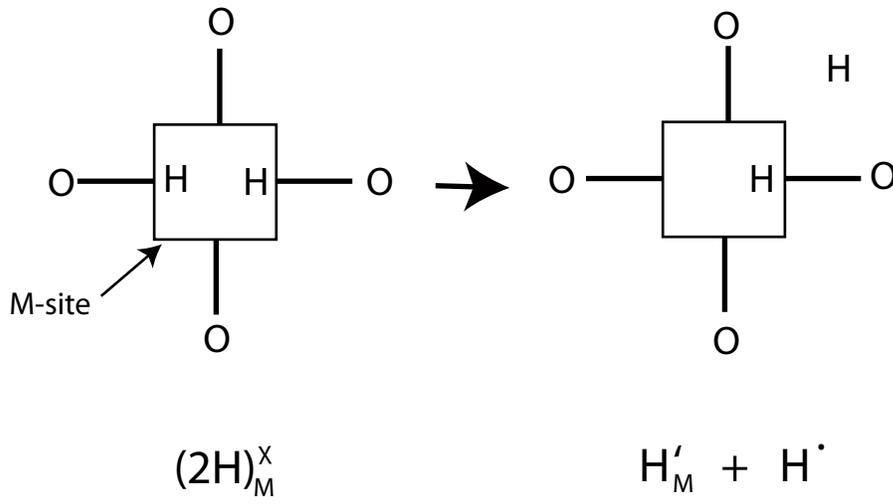


Fig. 8 (Karato-II)

(a) ionization of a neutral hydrogen-bearing defect



(b) energy level

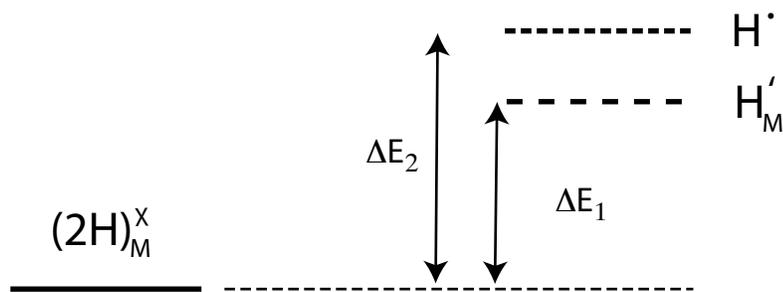
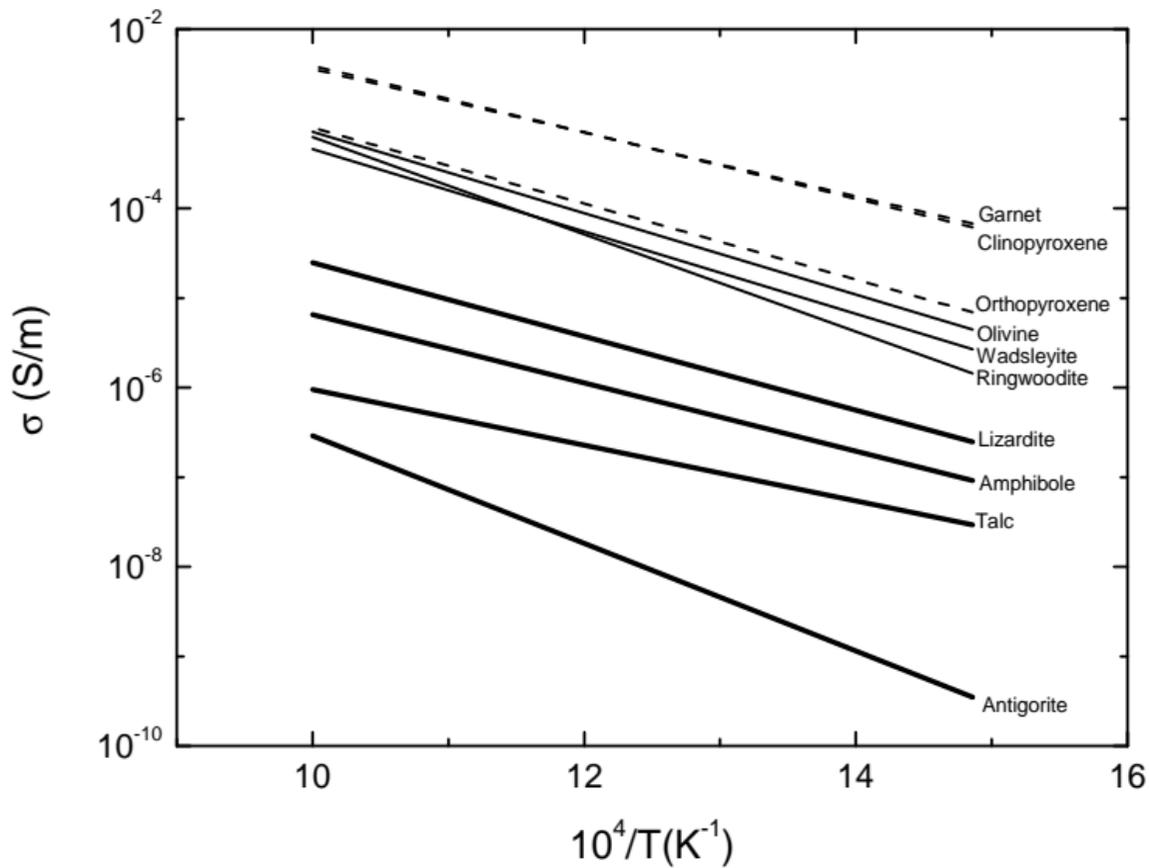


Fig. 9 (Karato-II)



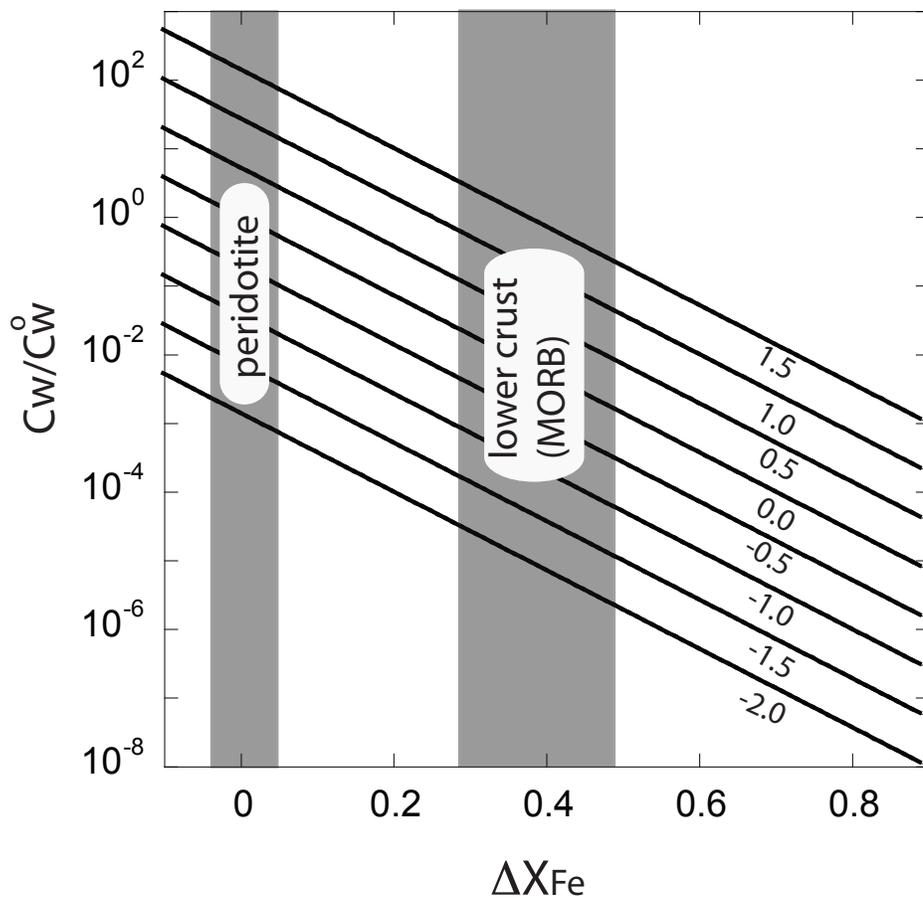


Fig. 11 (Karato-II)

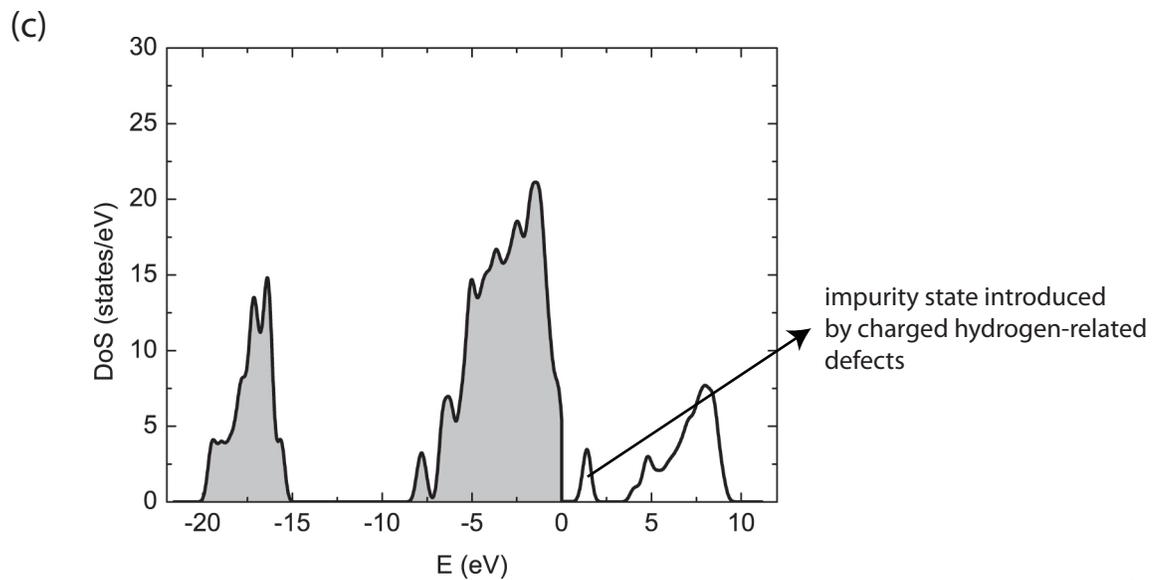
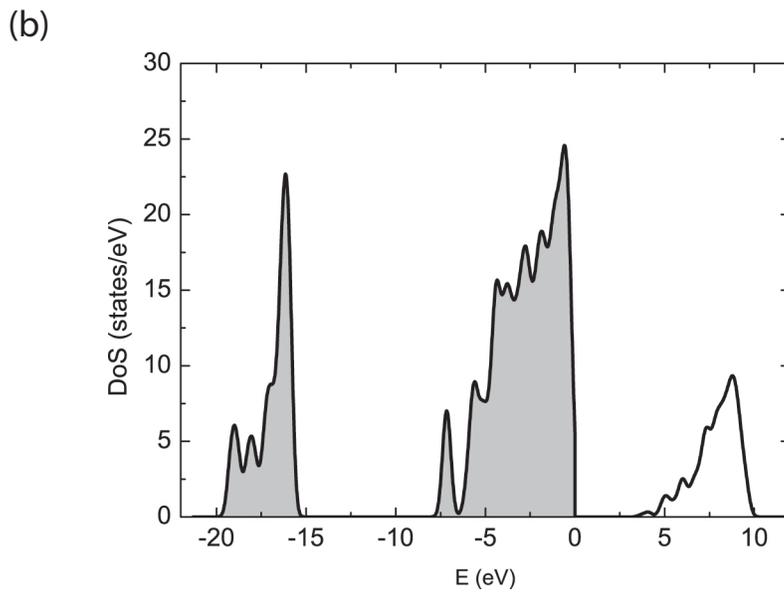
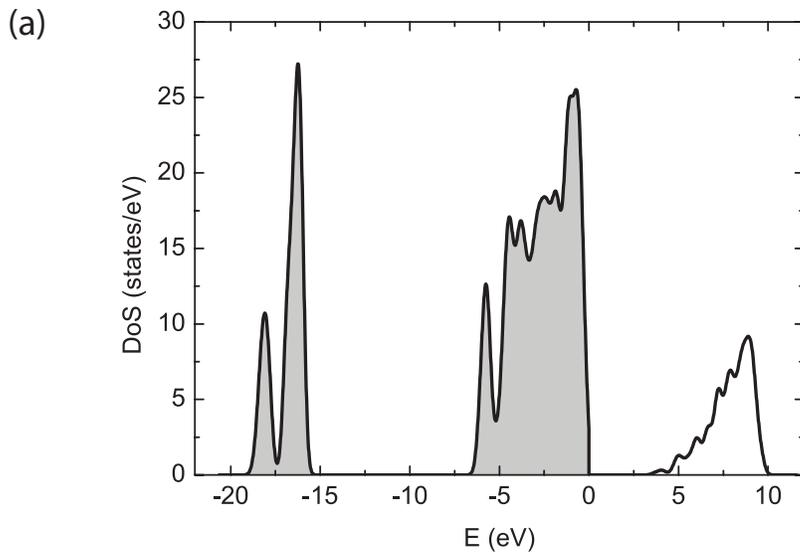


Fig. 12

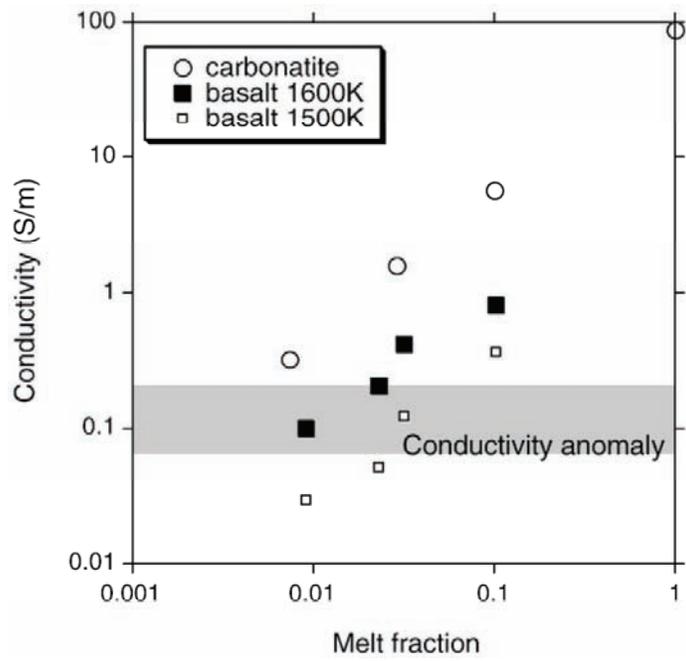


Fig. 13 (Karato-II)

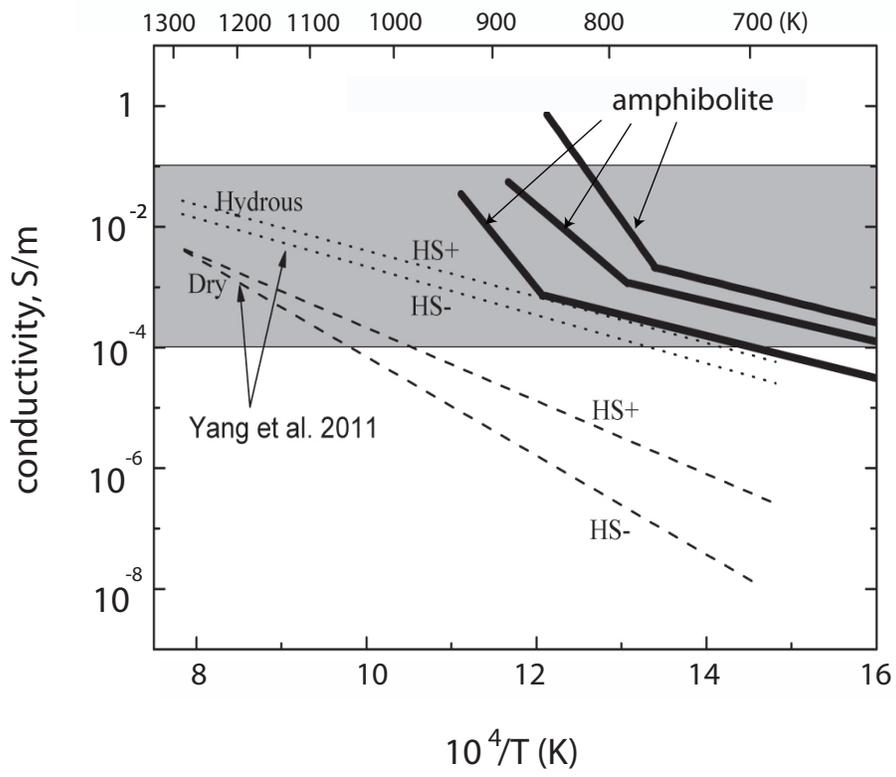
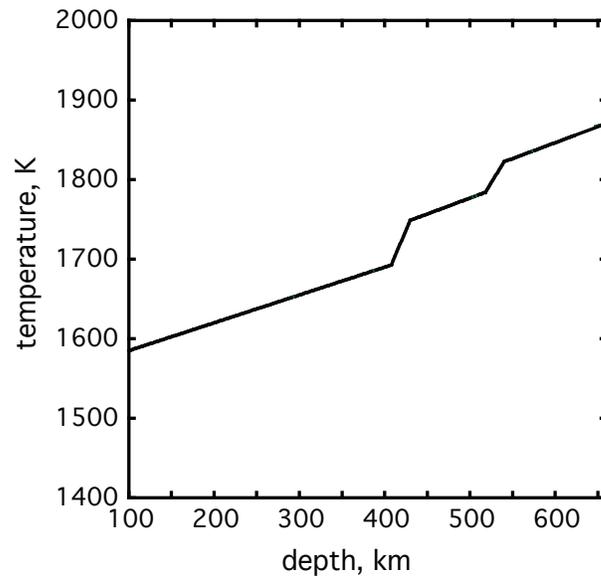


Fig. 14 (Karato-II)

(a)



(b)

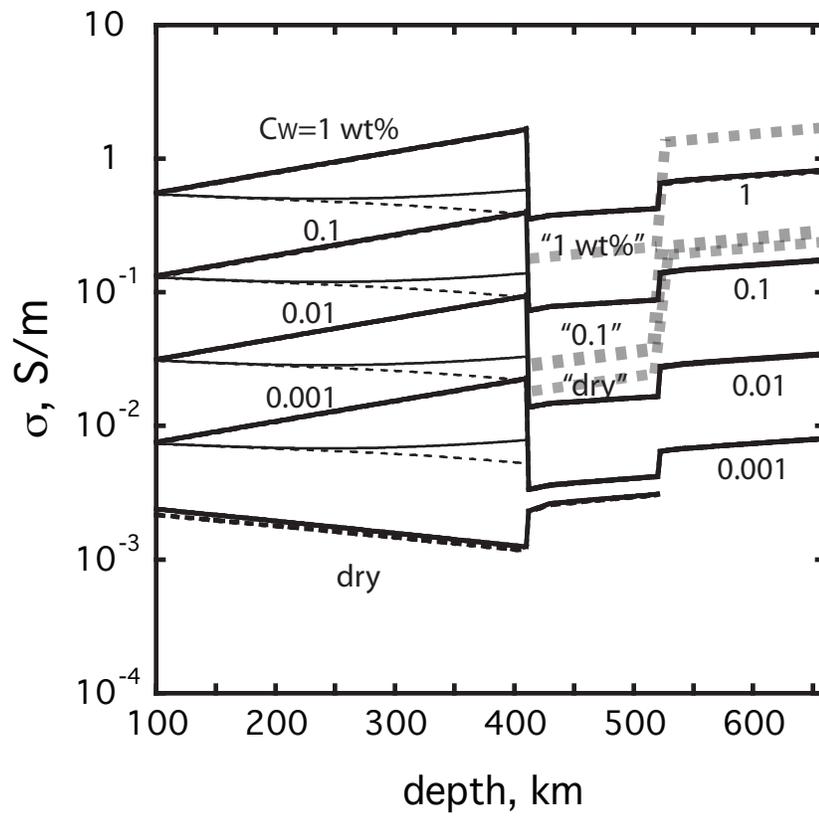


Fig. 15 (Karato-II)

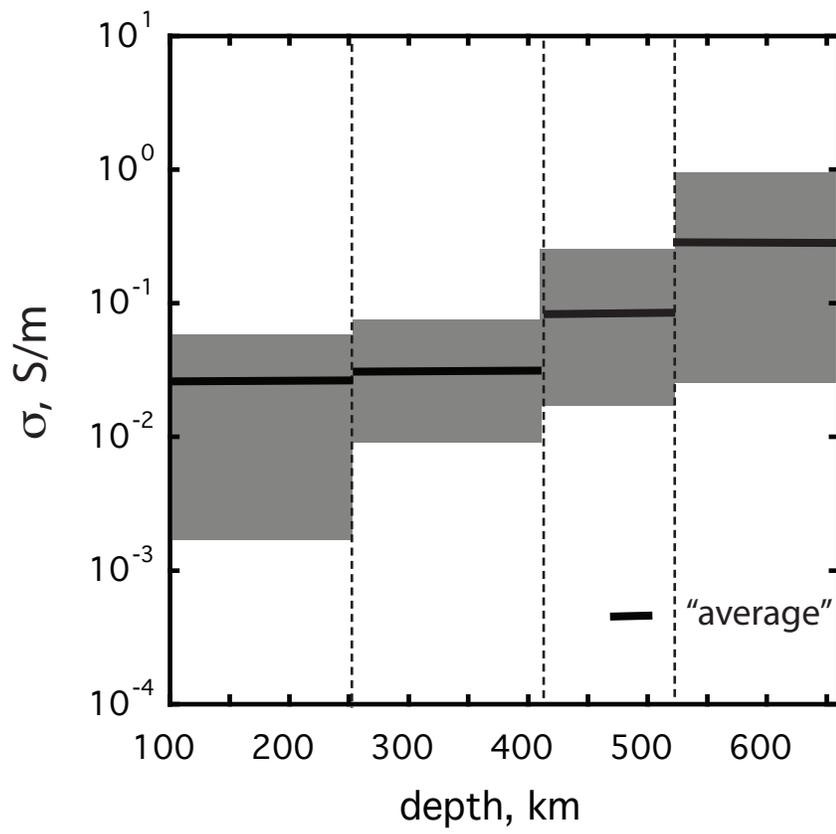
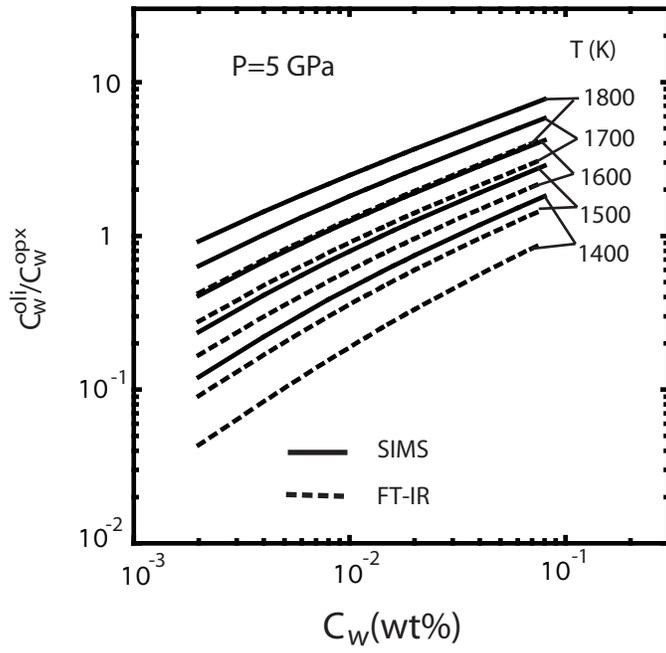


Fig. 16 (Karato-II)

(a)



(b)

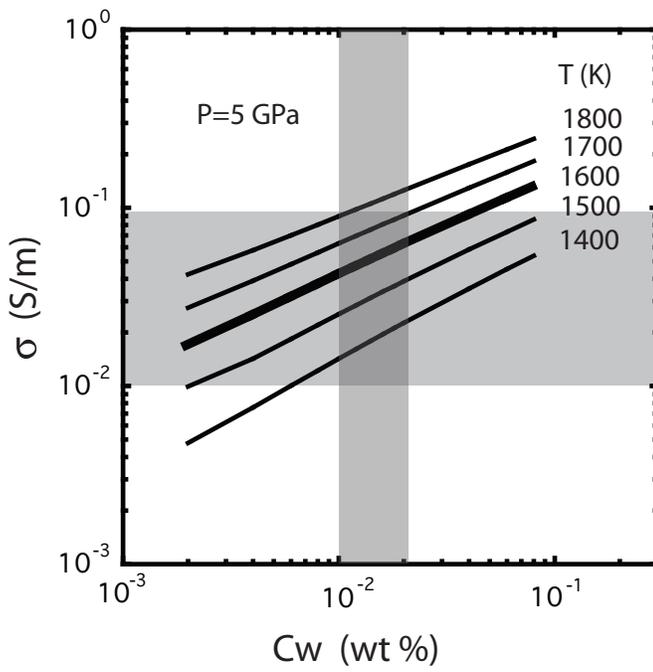


Fig. 17 (Karato-II)

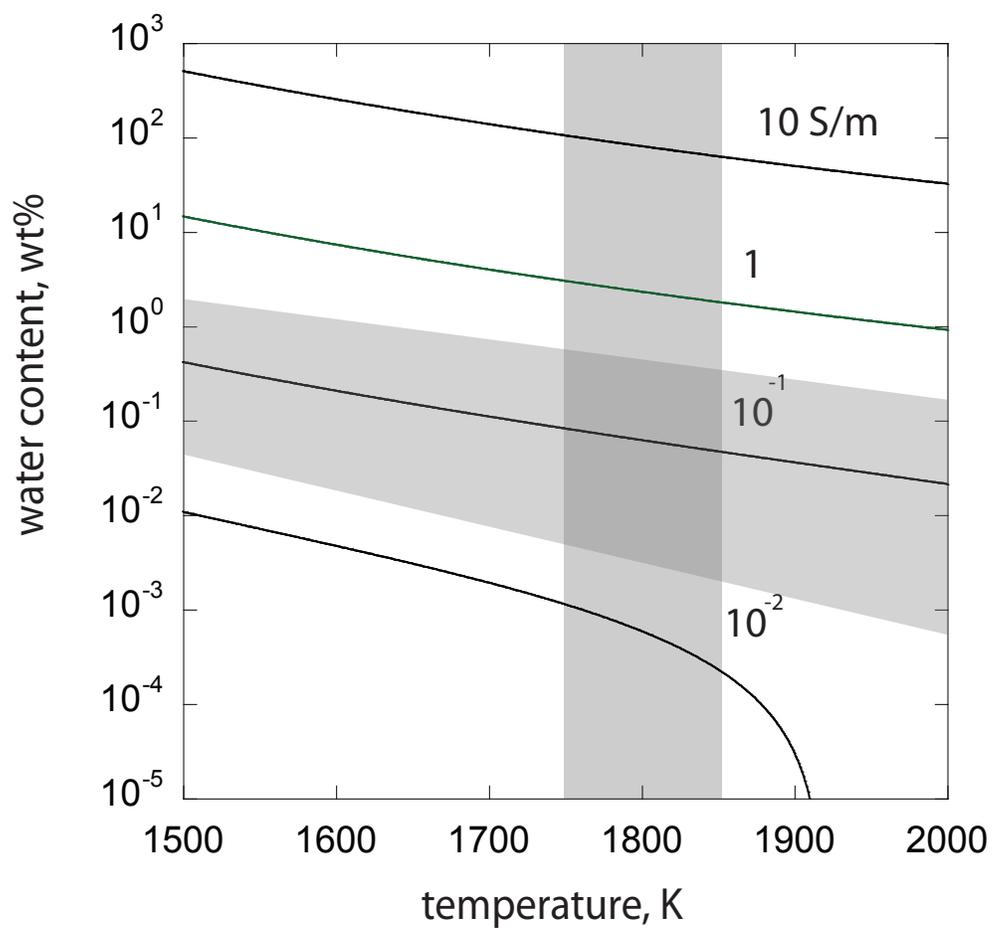


Fig. 18
(Karato-II)

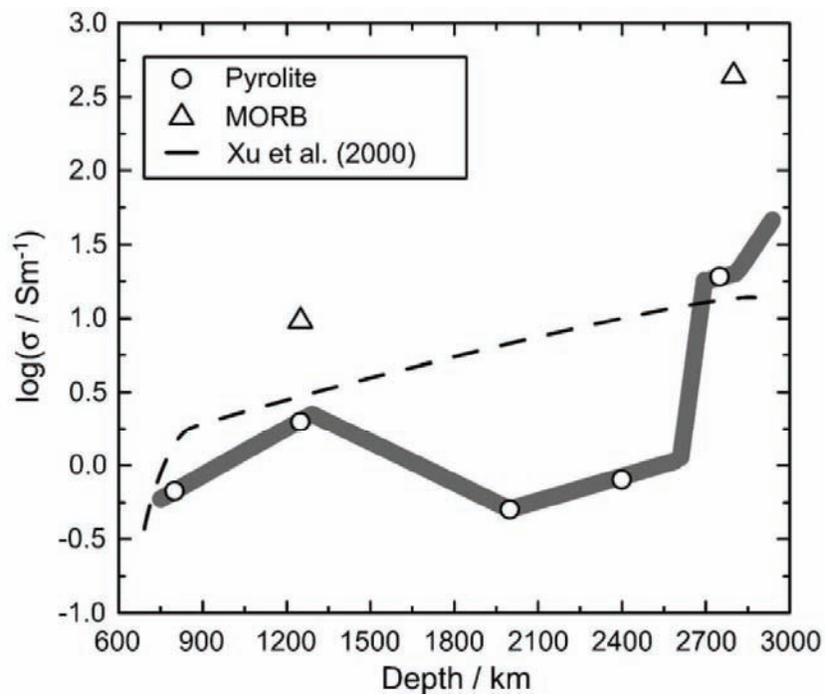
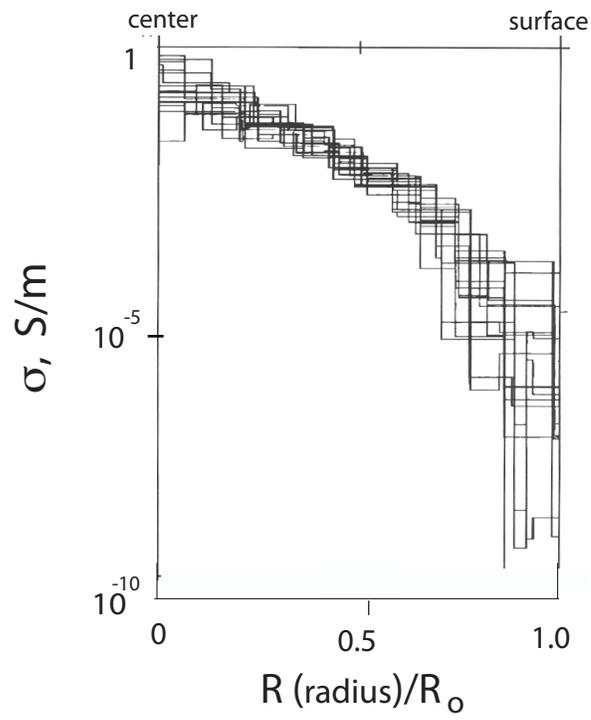


Fig. 19 (Karato-II)

(a)



(b)

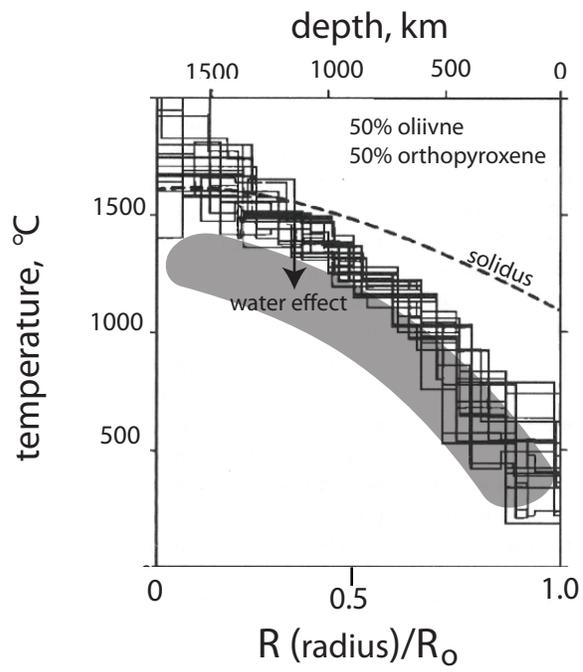


Fig. 20 (Karato-II)