CHAPTER 12

MICROSCOPIC MODELS FOR THE EFFECTS OF HYDROGEN ON PHYSICAL AND CHEMICAL PROPERTIES OF EARTH MATERIALS

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Abstract

Atomistic models of interaction of hydrogen with silicates are reviewed. The most important mechanism of hydrogen dissolution in Mg (Fe)-bearing silicates is the replacement of Mg (Fe) with two protons (a vacancy at M-site trapping two protons ($(2H)_M^{\times}$)). Influence of hydrogen on phase diagrams can be understood from this model. In addition to this fully charge-compensated defect, charged defects are also created by the ionization of a neutral defect, $(2H)_M^{\times}$. Electrical conductivity is due to ionized defect, i.e., free proton. When the concentration of ionized, charged defects exceeds the concentration of charged defects under hydrogen-free environment, then the concentrations of defects at other sub-lattices is also modified leading to the enhancement of a range of properties that are controlled by the motion of defects at silicon or oxygen sub-lattice. The parameterization of creep law in terms of hydrogen content is summarized and applied to the estimation of upper mantle viscosity and fabric transitions. Current knowledge of influence of hydrogen on the rheological properties of deep mantle minerals is reviewed. The role of hydrogen in each mineral in the deep mantle is mineral-specific: solubility of hydrogen and its role in plastic deformation are quite different among the various minerals in the transition zone and the lower mantle. Possible roles of hydrogen in deep Earth dynamics are discussed including the effects of hydrogen on the structure of plumes.

1 INTRODUCTION

Hydrogen is a unique element in terrestrial planets. It occupies only a very small mass fraction of any terrestrial planets (for Earth it occupies less than 0.01 wt%). Yet it has large influence on various physical and chemical properties of Earth materials including melting relations and rheological properties: addition of hydrogen reduces the melting temperature and reduces the rock's resistance to plastic flow (viscosity).

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These two properties are the key to the evolution and dynamics of terrestrial planets, and consequently understanding how hydrogen affects these properties is an important challenge to Earth scientists. This chapter provides a brief review of this subject with emphasis on the latest advances.

At a qualitative or semi-quantitative level, the effects of hydrogen on melting temperature and rheology have been well known for more than ~30 years (melting: Inoue and Sawamoto, 1992; Kusiro et al., 1968; rheology: Karato, 1989; Karato and Jung, 2003; Mei and Kohlstedt, 2000b; Paterson, 1989). The addition of hydrogen (water)[1] to a peridotite reduces the solidus by several hundred degrees, and the addition of hydrogen reduces the creep strength of many silicates more than an order of magnitude.

However, some important details remained unknown until quite recently. They include (i) the influence of hydrogen on phase diagrams such as the one for the olivine-wadsleyite transformation and (ii) the quantitative relationship between hydrogen content and various physical properties such as electrical conductivity, viscosity and seismic wave velocities for upper mantle minerals. In addition, new discoveries have been made on the effects of hydrogen including the high but variable solubility of hydrogen in silicate minerals (e.g., Ingrin and Skogby, 2000), the enhancement of electrical conductivity (Huang et al., 2005; Karato, 1990) and the changes in deformation fabrics in olivine by hydrogen (Jung and Karato, 2001b; Karato, 1995; Katayama et al., 2004). Furthermore the influence of hydrogen on properties of deep mantle minerals is almost unexplored. In addressing these issues, it is critical to understand the atomistic mechanisms by which hydrogen interacts with silicate minerals and melts. The purpose of this chapter is to present a review of our understanding of interaction between hydrogen and silicates at the atomistic level with the emphasis on those in solid silicates. I will first review the models of dissolution of hydrogen in silicates, and then review our current understanding of the way in which hydrogen affects various physical and chemical properties of Earth materials.

2 SOLUBILITY MECHANISMS

The first step in investigating the role of hydrogen in modifying the physical and chemical properties is to understand the mechanisms of dissolution of hydrogen in a given material. In silicates, hydrogen has a strong tendency to be associated with oxygen. In fact for silicate melts, H_2O and OH^- are the only species that are considered in modeling silicate melts (e.g., Burnham, 1979; Silver and Stolper, 1985). However, in silicate minerals, where structures are less flexible than those of melts, free water and free OH^- are less abundant and most of the hydrogen atoms are associated with cation-site vacancies or it could occur as free proton (e.g., Karato, 1989; Paterson, 1989).

[1] The author uses a term "hydrogen" throughout this chapter to indicate that it is hydrogen and not oxygen that affects the physical and chemical properties of silicates. In the literature, the term "water" is used more frequently.

2.1 Hydrogen (water) in silicate melts

For silicate melts, it is often assumed that hydrogen-related species is present either as molecular water (H_2O) or OH^- and an internal chemical equilibrium

$$[H_2O] + [O^{2-}] = 2[OH^-], \tag{1}$$

is considered (e.g., Burnham, 1979; Silver and Stolper, 1985). The concentration of oxygen atoms is assumed to be independent of oxygen fugacity. This is equivalent to the assumption that the charge balance is maintained only by O^{2-} and OH^-. This is in contrast to the case for silicate minerals in which the concentration of hydrogen-related defects is closely related to those of other charged defect species such as ferric iron Fe_M^g or M-site vacancy V_M''.

With this assumption, applying the law of mass action to the following reaction,

$$H_2O\,(\textit{fluid}) \Leftrightarrow H_2O\,(\textit{melt}), \tag{2}$$

one has

$$[H_2O] \propto f_{H_2O}(P,T)\exp\left(-\frac{PV_{H_2O}}{RT}\right), \tag{3}$$

$$[OH^-] \propto f_{H_2O}^{\frac{1}{2}}(P,T)\exp\left(-\frac{PV_{OH}}{RT}\right) \text{ for small water content}([O^{2-}] \approx 1), \tag{4}$$

where f_{H_2O} is the fugacity of water and V_X is the volume change of melt associated with the relevant reaction. As can be seen from Equations (3) and (4), dominant hydrogen-related species in a silicate melt changes with pressure and temperature. Note that the volume change associated with the dissolution of hydrogen-related species likely changes with pressure. The partial molar volume of water at $\sim$1 GPa is $\sim 16 \times 10^{-6}$ m^3/mol (Ochs and Lange, 1997) but it is $\sim 8 \times 10^{-6}$ m^3/mol at $\sim$14 GPa (Matsukage et al., 2005). This has important influence on the melt density as well as the pressure dependence of solubility of hydrogen-related species in melts.

An important recent finding in this area is that water and silicate melt becomes completely miscible above a certain pressure (and temperature) (Mibe et al., 2002). Defining thermodynamic properties of hydrous silicate melts is critical to the understanding of influence of hydrogen on melting (see Section 3.2).

2.2 Hydrogen in solid silicate minerals

Solubility mechanisms of hydrogen in solid silicates are quite different from those in silicate melts. Theoretical analysis of hydrogen-related defects in silicate was made by. (Karato, 1989; Kohlstedt et al., 1996; Mei and Kohlstedt, 2000a; Yan, 1992). Similar to melts, one can consider dissolution of free water (water molecule in the interstitial site of a crystal) or OH^-; but in the case of OH^- one must distinguish OH^- at interstitial site from that at the normal oxygen site. One major difference between

melts and solid silicates is that the structure of solid silicates is more compact, and consequently, there is not much "space" so that hydrogen is often associated with point defects. Considering the fact that the charge neutrality is a strict requirement in any chemical reactions, one can consider five models of dissolution of "water" in silicates containing two types of cations (e.g., Mg_2SiO_4) (Fig. 1):

(i) molecular water at an interstitial site
(ii) two protons from one molecule of water go to M-site, and Mg (or Fe, Ca) from M-site and one oxygen from water goes to the surface
(iii) four protons from two molecules of water go to Si-site, and Si from the Si-site and two oxygens from two water molecules (SiO_2) go to the surface
(iv) two protons go to two O-site oxygens, and one oxygen from water molecule goes to an interstitial site
(v) water reacts with an interstitial oxygen to create an interstitial OH^-.

For each mechanism, one can write an equation for chemical reaction as:

$$H_2O\,(fluid) \Leftrightarrow H_2O_I \qquad \text{for reaction (i)} \qquad (5)$$

$$H_2O\,(fluid) + M_M^{\times} \Leftrightarrow (2H)_M^{\times} + MO \qquad \text{for reaction (ii)} \qquad (6)$$

$$2H_2O\,(fluid) + Si_{Si}^{\times} \Leftrightarrow (4H)_{Si}^{\times} + SiO_2 \qquad \text{for reaction (iii)} \qquad (7)$$

$$H_2O\,(fluid) + 2O_O^{\times} \Leftrightarrow 2\,(OH)_O^{g} + O_I'' \qquad \text{for reaction (iv)} \qquad (8)$$

$$H_2O\,(fluid) + O_I'' + V_O^{gg} \Leftrightarrow 2\,(OH)_I' + V_O^{gg}, \qquad \text{for reaction (v)} \qquad (9)$$

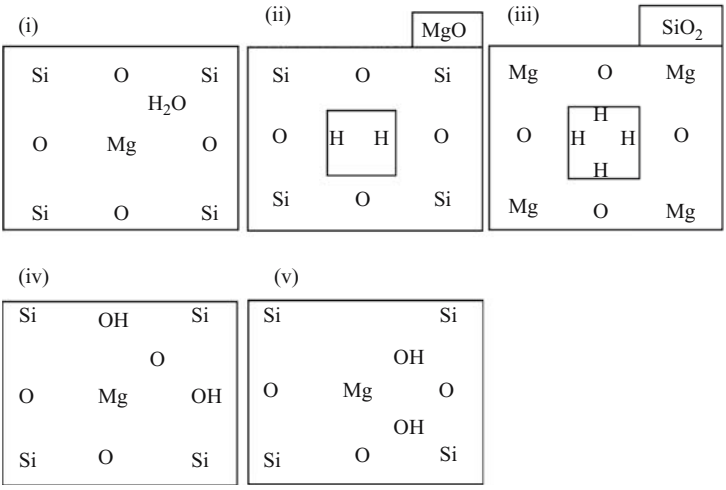


Figure 1. Mechanisms of dissolution of water (hydrogen) in silicates. Note that mechanisms (ii) and (iii) are associated with an explicit volume change. A volume change also occurs to a lesser extent in mechanisms (i), (iv) and (v).

where the Kröger-Vink notation of point defects is used, i.e., X_Y^Z means a species X occupying the Y-site whose effective charge is Z. The effective charge is defined relative to the perfect lattice and a cross means a neutral charge, prime a negative charge and a dot a positive charge.

The law of mass action can be applied to each reaction to yield

$$C_{\mathrm{H}} \propto C_w \propto f_{\mathrm{H_2O}}\,(P,T)\exp\left(-\frac{E_i + PV_i}{RT}\right), \tag{10}$$

$$C_{\mathrm{H}} \propto C_w \propto f_{\mathrm{H_2O}}\,(P,T)\,a_{\mathrm{MO}}^{-1}\exp\left(-\frac{E_{ii} + PV_{ii}}{RT}\right), \tag{11}$$

$$C_{\mathrm{H}} \propto C_w \propto f_{\mathrm{H_2O}}^{2}\,(P,T)\,a_{\mathrm{SiO_2}}^{-1}\exp\left(-\frac{E_{iii} + PV_{iii}}{RT}\right), \tag{12}$$

$$C_{\mathrm{H}} \propto C_w \propto f_{\mathrm{H_2O}}^{\frac{1}{2}}\,(P,T)\left[\mathrm{O}_{\mathrm{I}}''\right]^{\frac{-1}{2}}\exp\left(-\frac{E_{iv} + PV_{iv}}{RT}\right), \tag{13}$$

$$C_{\mathrm{H}} \propto C_w \propto f_{\mathrm{H_2O}}^{\frac{1}{2}}\,(P,T)\left[\mathrm{O}_{\mathrm{I}}''\right]^{\frac{1}{2}}\exp\left(-\frac{E_{v} + PV_{v}}{RT}\right), \tag{14}$$

where $C_{\mathrm{H}}(C_w)$ is the concentration of hydrogen (water) in the mineral, $f_{\mathrm{H_2O}}\,(P,T)$ is the fugacity of water that changes with pressure and temperature, a_{MO}, $a_{\mathrm{SiO_2}}$ are the activity of oxides, E_X is the energy change and V_X is the volume change of a solid associated with each reaction, X. Note that both $f_{\mathrm{H_2O}}\,(P,T)$ and $\exp(-(E_x + PV_x)/RT)$ terms strongly depend on pressure (and temperature) and they change with pressure in the opposite ways. Consequently the pressure dependence of hydrogen solubility is controlled by a delicate balance of these two terms. Note also that the concentration of OH^- (Eqs. (13) and (14)) depends on the number of oxygen interstitial atoms that in turn depends on thermo-chemical conditions.

For olivine, Zhao et al. (2004) determined the temperature (and pressure) dependence of hydrogen solubility to get $E_X \sim 50$ kJ/mol and $V_X \sim 10 \times 10^{-6}$ m^3/mol. Note that this value of V_X agrees well with the molar volume of MgO that is consistent with the model (i) above. For wadsleyite, Williams and Hemley (2001) proposed based on highly scattered data that hydrogen solubility *decreases* with temperature. Demouchy et al. (2005) showed that the hydrogen solubility in wadsleyite is only weakly dependent on temperature and pressure in the temperature range in which coexisting fluid is nearly pure water. Using the pressure and temperature dependence of water fugacity, this observation implies that for wadsleyite, we can estimate that $E_X \sim -(50\text{–}80)$ kJ/mol and $V_X \sim (11\text{–}13) \times 10^{-6}$ m^3/mol. Again, the estimated volume change, V_X, is roughly consistent with the volume of MgO supporting the mechanism (i)[2].

[2] Based on the observation of weakly pressure dependence of hydrogen solubility, (Demouchy et al., 2005) argued that the volume change associated with hydrogen dissolution in wadsleyite is nearly zero (which would be *inconsistent* with the model (i)). This inference is incorrect. The pressure dependence of water fugacity must be included in estimating V_X. Similarly, the temperature dependence of water fugacity needs to be included in estimating E_X.

The large difference in E_X between olivine and wadsleyite likely reflects the difference in crystal chemistry as first noted by (Smyth, 1987) (wadsleyite structure favors dissolution of hydrogen).

A comparison of these relationships with experimental observations on hydrogen solubility, as well as the experimental observations of infrared spectroscopy provides a clue as to the dominant defect-type under a given thermo-chemical condition. For quartz (and garnet), the mechanism (iii) i.e., the replacement of Si with four protons is the most important mechanism of hydrogen dissolution (e.g., Cordier et al., 1994; Doukhan and Paterson, 1986), whereas in Mg- (or Fe-) bearing silicate such as olivine, wadsleyite and orthopyroxene, mechanism (ii), i.e., the replacement of two protons with Mg (or Fe) is the most important mechanism of hydrogen dissolution (e.g., Kohlstedt et al., 1996). In the following, I will focus on this particular mechanism since most of minerals we will deal with contain Mg (Fe). Note, however, that the dominant defect type may change when thermo-chemical conditions are changed.

Several comments may be made here. (1) In an earlier study by Bai and Kohlstedt (1993), they investigated the mechanisms of hydrogen dissolution through two-stage thermo-chemical treatment in which a single crystal of olivine was first annealed at high temperatures (∼1573 K) for a given oxygen fugacity and oxide activity. Then the crystal was annealed at lower temperatures (∼1173–1323 K) under hydrous conditions. In this treatment, it is believed that the non-stoichiometry (i.e., Mg/Si, Mg + Fe/O ratios) of a sample is equilibrated with the thermo-chemical conditions in the first stage treatment, and in the second stage, hydrogen reacts with an olivine with fixed stoichiometry. Based on the dependence of concentration of hydrogen on oxygen fugacity and oxide activity in the first stage, Bai and Kohlstedt (1993) concluded that the reaction (v) is the dominant mechanism of hydrogen dissolution in olivine. The distribution of hydrogen after this type of thermo-chemical treatment is only partially in chemical equilibrium with the environment, and the results of such an experiment do not necessarily correspond to the atomic mechanisms of hydrogen dissolution at chemical equilibrium. (2) A proton is in most cases attracted to an oxygen ion to form an OH^- dipole. This is the case even for mechanisms (ii) and (iii). To illustrate this point, a defect such as $(2H)_M^\times$ may be written as $\{(OH)_O^\bullet - V_M'' - (OH)_O^\bullet\}^\times$, but this notation obscures the site of a defect. This defect is primarily associated with the M-site and therefore changes the configuration entropy of the system through its effects on the M-site. (3) Throughout this paper, I will use the values of hydrogen contents determined by infrared spectroscopy using the Paterson calibration (Paterson, 1982). There are new calibrations on olivine that suggest that the Paterson calibration may need some corrections (e.g., Bell et al., 2003). However, new calibration is available only for olivine but not for other minerals such as wadsleyite. At the lack of any experimental data showing otherwise, I assume that the corrections are similar for all minerals, so the new calibration will not affect most of the conclusions in this paper except for the absolute values of water (hydrogen) content because all the data are data based on the same calibration.

3 INFLUENCE OF HYDROGEN ON THE PHASE DIAGRAMS

Given the solubility mechanisms of hydrogen in melts and solid minerals, one can make a theoretical analysis of phase relationships such as solid-solid phase transformations or melting. The construction of such a phase diagram depends critically on the expression of a relationship between the hydrogen content and the chemical potential that is determined by the atomistic mechanism of hydrogen dissolution.

3.1 Influence of hydrogen on the olivine-wadsleyite phase boundary

Dissolution of hydrogen reduces the free energy of a material. Experimental studies show that a significantly larger amount of hydrogen can be dissolved in wadsleyite than in olivine (e.g., Kohlstedt et al., 1996; Young et al., 1993). Therefore the dissolution of hydrogen will expand the stability field of wadsleyite relative to that of olivine (the depth of "410-km" boundary will be shallower if a large amount of hydrogen is present). A more subtle effect is the change in the *width* of the "410-km" discontinuity with hydrogen content. When the system is considered to be a binary system, i.e., Mg_2SiO_4-Fe_2SiO_4, there is a range of pressure (at a fixed temperature) during which the phase transformation is completed. When the upper and the lower boundaries are affected by hydrogen differently, then the width of the boundary will be modified by hydrogen.

The degree to which the dissolution of hydrogen affects the free energy depends on the atomistic mechanisms of hydrogen dissolution. In his paper on this topic, (Wood, 1995) used a model of hydrogen dissolution in wadsleyite by (Smyth, 1987, 1994) and in olivine by Bai and Kohlstedt (1993). These models are not consistent with the recent experimental observations as summarized in Section 2, and here I use a model that is consistent with the current experimental observations as discussed in Section 2. In my model, the dissolution mechanism is identical for both olivine and wadsleyite, hydrogen is dissolved mainly as $(2H)_M^{\times}$, and only the magnitude of solubility is different between the two phases. In calculating the phase diagram, I use a simplifying assumption that the system under consideration can be treated as an ideal mixture of three components, Mg, Fe and H for the M-sites. In this approximation, the chemical potential of each component is a function of concentration of each component as

$$\mu_{ij} = \mu_{ij}^0 + RT \log x_{ij}, \tag{13}$$

where μ_{ij} is the chemical potential, μ_{ij}^0 is the chemical potential for a pure material and x_{ij} is the mole fraction of M-sites for a component i (Mg, Fe and H) in phase j (olivine and wadsleyite). Chemical equilibrium demands

$$\mu_{io}^0 + RT \log x_{io} = \mu_{iw}^0 + RT \log x_{iw} \quad \text{for } i = \text{Mg, Fe and H}, \tag{14}$$

where subscript $o(w)$ refers to olivine (wadsleyite). The M-site is shared by three elements so that

$$\sum_i x_{io} = \sum_i x_{iw} = 1. \tag{15}$$

There are six unknowns (three components in a two phase system) with five equations ((14) and (15)). Another necessary parameter is the water fugacity that determines the hydrogen content (in olivine, x_{Ho}). In the first calculation, I fixed the water fugacity, i.e., I assumed the *open system* behavior. I use the various values of hydrogen content in olivine (corresponding to the various values of water fugacity) and the ratio of water content in wadsleyite to olivine is fixed to be $x_{Hw}/x_{Ho} = 10$, which is assumed to be independent of pressure. (This is justifiable because in my model, the mechanism of hydrogen dissolution is identical between olivine and wadsleyite, but not valid for the model assumed by Wood, 1995.) Thermodynamic data for Mg and Fe components of olivine and wadsleyite are from Akaogi et al., 1989. The results are shown in Figure 2a, showing that the depth of transition decreases with the increase in hydrogen content. Both the upper and the lower boundaries move nearly the same amount, and the width of the transition does not change with hydrogen in this case (open system behavior).

When a phase transformation occurs in a *closed system* with hydrogen-undersaturated condition, then a progressive phase transformation will change the concentrations of hydrogen in each phase according to the degree of transformation (water

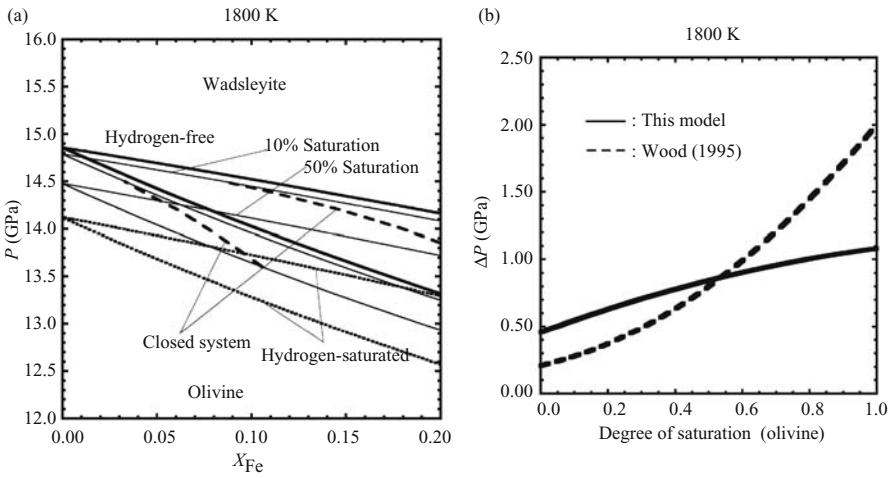


Figure 2. The influence of hydrogen on the olivine-wadsleyite phase boundary. (a) Solid lines: results for an open system. Broken curves: results for a closed system with the total water content of 50% saturation. (b) Variation of the width of the olivine-wadsleyite boundary with hydrogen saturation (saturation in olivine corresponds to ~0.1 wt% water or 1.5×10^4 ppm H/Si).

fugacity will change with the progress of a phase transformation). Consequently, when the pressure just reaches the minimum pressure at which the wadsleyite phase appears, much of the hydrogen is in olivine, whereas the hydrogen concentration in olivine decreases as the volume fraction of wadsleyite increases. Therefore the pressure at which olivine starts to transform to wadsleyite is controlled by the initial water content in olivine, and is significantly lower than the pressure at which this transformation would start in hydrogen-free system. In contrast, the pressure at which this transformation is completed is controlled by the hydrogen content in olivine at this stage that is significantly lower than the hydrogen content at the beginning of the olivine to wadsleyite transformation. (Exactly the same can be applied to a case when a phase transformation starts from wadsleyite.) A phase diagram for this more realistic case can be calculated from the results of fixed hydrogen content by incorporating the mass balance requirement (see broken curves in Figure 2a). As a result of this gradual change in hydrogen content in each phase, there is a broadening of the binary loop as first pointed out by Wood, 1995. The width of the olivine to wadsleyite binary loop calculated in this way is shown in Figure 2b. Note that although the width of the boundary increases with hydrogen content similar to the model by Wood (1995), the degree to which the width increases with hydrogen content is somewhat different between the present model and the model by Wood (1995). This difference is caused mainly by the difference in the model of hydrogen dissolution and the choice of thermodynamic parameters.

A few comments are in order here. (1) The model results for an open, saturated system agree with the experimental observations by Chen et al. (2002); Smyth and Frost (2002) for an open, water-saturated system. But the close system behavior predicted by the model has not been tested experimentally. Chen et al. (2002); Smyth and Frost (2002) compared their results for an open system directly with those by Wood (1995) for a closed system and discussed that their results did not agree with those by Wood (1995). This is misleading. The variation of the width of transformation by hydrogen content predicted by Wood (1995) model occurs only in a closed system but not in an open system. (2) The validity of the assumption of a closed system behavior in real Earth is not necessarily obvious. If the amount of water (hydrogen) in Earth's transition zone exceeds a critical value ($\sim$0.05 wt% , see the next section), the phase transformation from wadsleyite to olivine in a upwelling current could cause partial melting (Bercovici and Karato, 2003). In this case, hydrogen can be removed from the system during the phase transformation and the assumption of a closed system behavior will be violated. (3) A comparison of the model results on the width of the "410-km" boundary with seismological observation is not straightforward due to the fact that the actual depth variation of acoustic properties in a phase loop may not a simple function of the volume fraction of each phase (Stixrude, 1997). In summary, I conclude that the use of the width of the "410-km" discontinuity to infer the water (hydrogen) content as proposed by Wood (1995) (see also van der Meijde et al., 2003) is subjected to large uncertainties. Other techniques such as the use of electrical conductivity or seismic wave velocities (or attenuation) provide a more robust estimate of hydrogen contents (e.g., Karato, 2003; Huang et al., 2005).

3.2 Influence of hydrogen on the melting relation in the olivine- and wadsleyite-rich systems

A similar consideration suggests that the boundary between a solid mineral and a melt should be modified by the addition of hydrogen (water). Whatever the details might be, the addition of hydrogen should expand the stability field of melt and reduces the solidus temperature because a significantly larger amount of hydrogen is dissolved in a melt than in a solid.

Here I will discuss the influence of hydrogen on the melting relation for olivine- and wadsleyite-dominated systems. A particularly interesting issue here is the estimate of the critical amount of water (hydrogen) needed to initiate melting under deep upper mantle conditions which determines the plausibility of the transition-zone melting hypothesis (e.g., Bercovici and Karato, 2003).

A schematic phase diagram of silicate (olivine- or wadsleyite-rich) and water (hydrogen) system is shown in Figure 3. At low temperatures, a fluid phase that coexists with a silicate (olivine or wadsleyite) is more-or-less pure H_2O. Therefore the phase diagram at the lower temperature should be a diagram in which two phases (olivine (wadsleyite) and water) has small mutual solubility. The solidus at low temperatures corresponds, approximately, to the solubility limit of water (hydrogen) in olivine (wadsleyite). The water (hydrogen) solubility in olivine increases with temperature (Zhao et al., 2004). Therefore the solidus for olivine should have a positive slope on a water content versus temperature plane. The intrinsic temperature effect of water (hydrogen) solubility in wadsleyite is not known (see for discussion on this issue, Demouchy et al., 2005); but it is expected to be smaller than olivine because the enthalpy of dissolution of water (hydrogen) in wadsleyite is likely to be smaller than that in olivine. Above a certain temperature, the composition of a fluid phase that coexists with olivine (wadsleyite) changes drastically with temperature: the solubility of silicates in aqueous fluids increases with temperature (also with pressure) (e.g., Mibe et al., 2002). Consequently, the activity of water (hydrogen) in a fluid phase coexisting with olivine or wadsleyite decreases with increasing temperature. This causes the decrease in water (hydrogen) content in olivine or wadsleyite with temperature; and eventually, the curve must go to zero water content at a temperature corresponding to the melting temperature at water-free condition ($\sim$2500 K at $\sim$13 GPa for olivine[3]). Therefore the solidus must have a kink or an inflection point at a certain temperature above which the temperature dependence of silicate content in a fluid is important. If the location of this kink (the inflection point) corresponds to the eutectic point reported by Inoue (1994), then this temperature is $\sim$1500 K at $\sim$13 GPa and the water content in olivine at this point is $\sim$0.1 wt% (I use the temperature and pressure dependence of water (hydrogen) solubility based on Zhao et al. (2004)). The exact calculation of the solidus above this point is difficult because

[3] This temperature is significantly lowered ($\sim$500 K) when the influence of other volatiles such as carbon dioxide is included.

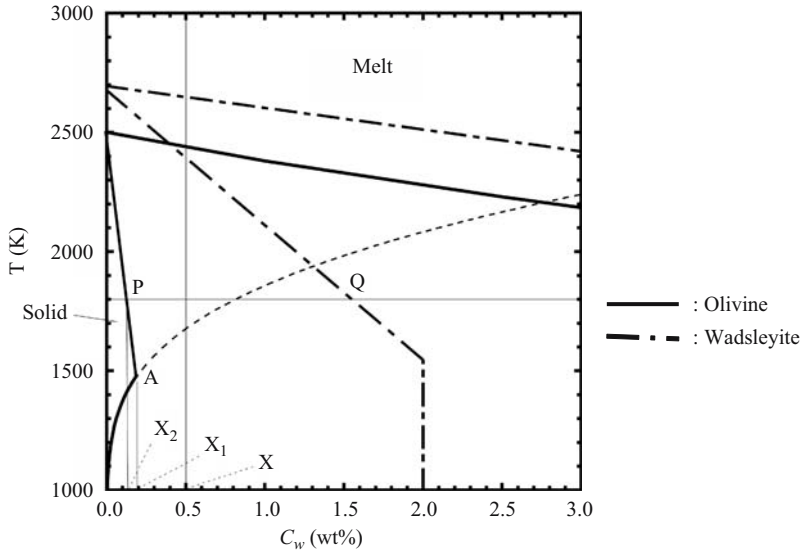


Figure 3. Influence of hydrogen (water) on the melting relationship in an olivine- or wadsleyite-rich system at ~400–450 km depth. Only a silicate-rich portion is shown. The low temperature part of the phase diagram is constrained by the solubility data. The inflection point, A, is constrained by the phase relationship determined by Inoue (1994) and the solubility data by Zhao et al. (2004) to be $X_1 \sim 0.1$ wt% and $T \sim 1500$ K. If the initial water content is $X \sim 0.1 - 1$ wt%, an upwelling material ($T \sim 1800$ K) in the wadsleyite-dominant region will not melt since the boundary between solid and melt for wadsleyite is at the water-rich side (Q). As the material ascends, the volume fraction of olivine increases and the boundary shifts to the water-poor side (P). If this melt-solid boundary intersects a line for a given water content (X), then partial melting will occur. The critical water content for melting is estimated to be $X_2 \sim 0.05$ wt% or less.

we do not know the dependence of free energy of a hydrous silicate melt on water (hydrogen) content precisely.

Although the phase diagram of this system is not precisely known at this time, a useful constraint can be obtained about the critical water (hydrogen) content for partial melting. Imagine an upwelling mass across the "410-km" boundary. The temperature in that mass follows more-or-less the adiabatic gradient (~0.3–0.4 K/km). For a typical mantle temperature, the temperature of an upwelling mass at 410-km is ~1800 K. Consider a rock mass initially in the wadsleyite-rich region (say at 450 km). Because the hydrogen solubility in wadsleyite is significantly higher than that in olivine, the solidus for wadsleyite should be in the water (hydrogen)-rich side. For a typical water content in the transition zone (~0.1 wt%, Huang et al., 2005), water content-temperature conditions will be to the "left" of the curve in this phase diagram, and melting will not occur in a wadsleyite-dominated region. As the volume fraction of wadsleyite decreases with further upwelling, the solidus shifts to the lower water content, and eventually partial melting will occur. Therefore the critical water

content for partial melting is defined by the intersection of a mantle adiabat with the solidus for an olivine-rich system. If Inoue (1994)'s eutectic point and water-free melting points are used, I estimate that this critical water content is ~0.05 wt% or less for an adiabat of ~1800 K. The precise value of X_2 is difficult to constrain because of the lack of detailed knowledge about the thermodynamic properties of hydrous silicate melt under these conditions.

Note also that the estimate of the melting relation presented above is based on the assumption that only hydrogen is an element that enhances melting through the increase in configurational entropy. This is unlikely to be true, and the influence of other elements such as carbon (Dasgupta and Hirschmann, 2006) or potassium (Wang and Takahashi, 2000) should also be considered. In these cases, the conditions for melting are significantly expanded (see Karato et al., 2006).

These two examples illustrate how the knowledge of the dissolution mechanisms of water (hydrogen) may be used to investigate the phase relationships in mantle materials. In these cases, only the dominant hydrogen (water)-related defects play important roles. I conclude that the mechanisms of hydrogen dissolution in solid minerals are well understood and the influence of hydrogen on the phase diagram involving solid minerals is well constrained. In contrast, large uncertainties remain in our understanding of the influence of hydrogen on the free energy of melts.

In the next section, I will focus on the influence of hydrogen on the transport properties of solid minerals, which requires a deeper level of understanding of materials science including the influence of minor hydrogen-related defects.

4 EFFECTS OF HYDROGEN ON DEFECT-RELATED PROPERTIES OF MINERALS

4.1 Point defects

The solubility mechanisms of hydrogen summarized in Section 2 show that in most cases, the majority of the hydrogen is incorporated in minerals as fully charge-compensated defects associated with one particular cation (Mg (Fe), Ca or Si) in a mineral. As far as these defects are neutral (relative to the perfect crystal), the chemical reaction is closed in a particular sub-lattice, and the dissolution of hydrogen does not affect the concentration of defects at other sites. In this regime, the dominant defects that define the charge balance in Fe-bearing minerals are ferric iron Fe^{g}_{M} and M-site vacancy V''_M through $[Fe^{g}_{M}] = 2[V''_M]$ (e.g., Karato, 1974). The defect population is determined basically by the oxidation-reduction reaction. I will call this as the *redox-controlled regime*. However, in reality, the dissolution of hydrogen not only results in neutral defects but also some charged defects through the following type of reaction,

$$(2H)^{\times}_{M} \Leftrightarrow H'_M + H^{g}, \tag{16}$$

where H'_M is a M-site vacancy containing one proton and H^{g} is a free proton.

There are two important consequences of this ionization reaction. First, once a large amount of charged defects such as H'_M are created, then the charge balance of a crystal is modified, and the concentrations of defects at other sub-lattice sites will also be affected. For a reasonable range of conditions, $[(2H)^{\times}_M]/[V''_M] \sim 10^2$–$10^3$, and in such a case, if more than ∼0.1–1 % of $(2H)^{\times}_M$ is ionized by the reaction (16), then the charge balance will be modified. Second, the dominant charge carrying species for electrical conduction will be a minor defect, H^g, if $[H^g]\mu_{H^g} > [(2H)^{\times}_M]\mu_{(2H)^{\times}_M}$ where μ_X is the mobility of a species X. The experimental study by Huang et al. (2005) showed

$$\sigma_{\text{cond}} \propto C_w^{3/4}, \tag{17}$$

where σ_{cond} is electrical conductivity. This result can be interpreted by the conduction due to free protons, H^g, but not by a dominant defect, $(2H)^{\times}_M$, with a charge neutrality condition of $[H'_M] = [Fe^g_M]$ (for conduction due to $(2H)^{\times}_M$, one expects $\sigma_{\text{cond}} \propto C_w$). This means that the ionization reaction is relatively easy although the dominant hydrogen-related species is $(2H)^{\times}_M$[4]. This indicates that the mobility of a free proton is much higher than that of a proton trapped at the M-site. Note that Karato (1990)'s proposal that the electrical conductivity can be directly calculated from the (total) hydrogen content and hydrogen diffusion coefficient using the Nernst-Einstein relation is not justified. Direct conductivity measurements are needed.

In this regime ($[H'_M] = [Fe^g_M]$), concentrations of all other defects are affected by the dissolution of hydrogen. I will call this the *proton-controlled regime*. Consequently, concentrations of all other defects in this regime depend on hydrogen content in the crystal. Therefore plastic deformation that is likely dependent on the diffusion in Si- or O-sublattice is also enhanced by the presence of hydrogen. Figure 4 illustrates the dependence of point defects on chemical environment in these two cases.

The diffusion of atoms in a solid is related to the concentration and diffusivity of relevant defect. Therefore the influence of hydrogen on diffusion is through the effects on defect concentration and through its influence on mobility, viz.,

$$D(C_w) = x_d\,(C_w) \cdot D_d\,(C_w)\,, \tag{18}$$

where $x_d(C_w)$ is the concentration of defect (fraction of defects at a relevant site) and $D_d(C_w)$ is the diffusion coefficient of that defect. In principle, both of these factors can be affected by hydrogen. However, in most cases, the influence of hydrogen on $D_d(C_w)$ is weak, and most of the influence of hydrogen on diffusion is through $x_d(C_w)$ (Hier-Majumder et al., 2005). Consequently, results such as those shown in Figure 4 can be used to calculate the dependence of diffusion coefficients on hydrogen fugacity (or content).

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[4] This statement means that $[H'_M]?[V''_M]$ and in combination with the results by Hier-Majumder et al. (2005), ('Influence of protons on Fe-Mg interdiffusion in olivine', *Journal of Geophysical Research* **110**, 10.1029/2004JB003292), it implies $[(2H)^{\times}_M]?[H'_M]?[V''_M]$.

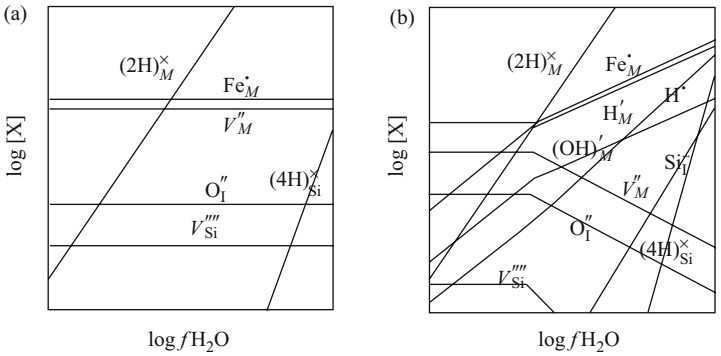


Figure 4. The point defect concentration versus water fugacity diagram for (a) a high ionization potential and (b) a low ionization potential. The Kröger-Vink notation of point defects is used. In case (a), all hydrogen-related point defects are neutral, and the dissolution of hydrogen in one sublattice (say M-sublattice) does not affect the point defect concentration in the other sublattice. In contrast, when the ionization potential is low, then the dissolution of hydrogen at the M-sublattice changes the population of charged defects and hence modifies the concentration of point defects in the other sublattices.

The results summarized above can be directly applied to plastic flow when the deformation is caused by the diffusion of atoms, i.e., diffusion creep. For example, a comparison of the dependence of the rate of deformation on water fugacity with the results of Figure 4 can provide a constraint on the atomic species that controls the rate of deformation. It should be noted that in identifying the atomistic mechanisms of diffusion from such a comparison, the proper parameterization incorporating the effects of both pressure dependence of the fugacity (of water) and the activation volume must be used. In the experimental study such as the one by Mei and Kohlstedt (2000a) at low pressures ($<$0.45 GPa), they could not constrain the activation volume term, and consequently it is difficult to identify the atomistic mechanisms of diffusion convincingly from studies at low pressures.

As can be seen in Figure 5, the dependence of the strain-rate on pressure under hydrogen-saturate conditions is non-monotonic, as was first pointed out by Karato (1989). The strain-rate first increases with pressure due to the effects of increasing water fugacity, but then at higher pressures it decreases with pressure if the activation volume is large. It is important to note that, without knowing the value of activation volume, no laboratory data can be extrapolated to the Earth's interior beyond a few tens of km ($>$1 GPa) (see Fig. 5). Experimental studies at pressures higher than $\sim$2 GPa are needed to place any meaningful constraints on the activation volume. A similar behavior was found by Hier-Majumder et al. (2005) in their study of Mg-Fe diffusion in olivine under hydrogen-saturated conditions to 6 GPa.

It should also be emphasized that in most high-pressure experiments, a large amount of hydrogen is dissolved in a sample even though hydrogen (water) is not added intentionally without a great care being taken (Huang et al., 2005; Nishihara et al.,

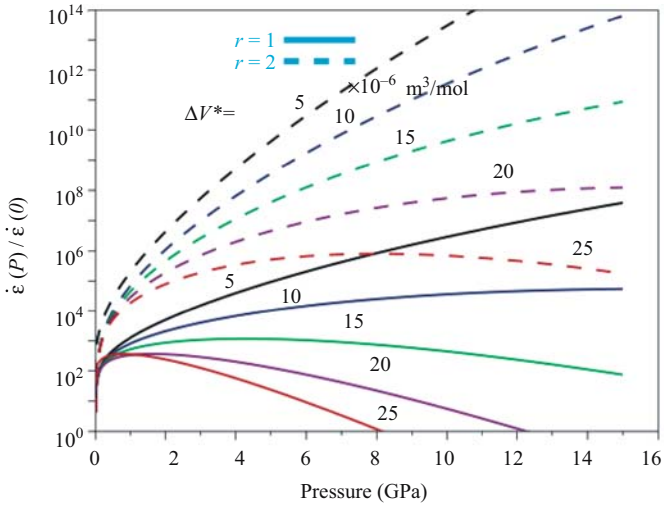


Figure 5. Influence of pressure on the rate of deformation under hydrogen-saturated conditions. The pressure dependence of rate of deformation is controlled both by the water fugacity and the activation volume as $\dot{\varepsilon} \propto f^{r}_{H_2O}(P,T)\exp(-P\Delta V^*/RT)$. Uncertainties in the activation volume, ΔV^*, cause major uncertainties in the estimated strain-rate above ~2 GPa. In other words, a robust constraint on activation volume can only be obtained by the experiments above ~2 GPa.

2006). Consequently, many of the published results on "pressure" effects on diffusion and deformation likely include significant influence of hydrogen. Unusually low activation volumes reported in many previous high-pressure experiments on diffusion (Béjina et al., 2003) or deformation (Li et al., 2004) ($<1\times10^{-6}$ m^3/mol) could be due to unrecognized large effects of hydrogen at high pressures. The hydrogen content in a sample before and after each experiment must be measured and reported in any high-pressure research in this area.

4.2 Dislocations

Dislocations play an important role in plastic deformation, seismic wave attenuation (hence seismic wave velocities) as well as in other kinetic processes such as the kinetics of phase transformation. Hydrogen is known to have a strong influence on dislocation mobility and hence on these physical processes. Currently, the best knowledge about the influence of hydrogen on dislocation mobility comes from the experimental studies of dislocation creep combined with theoretical studies on the interaction of hydrogen with dislocations. Previous papers reviewing the mechanisms of hydrogen effects (on dislocation creep) include Karato (1989) and Paterson (1989). Karato (1989) presented a model of the influence of hydrogen on point defects in olivine (as summarized in Sections 2 and 4.1) and also predicted a non-monotonic

effect of pressure under hydrogen-saturated conditions which is supported by the later experimental study of (Karato and Jung, 2003). Paterson (1989) reviewed the experimental observations and microscopic models of the weakening of quartz by hydrogen. Here I will review the issue of the influence of hydrogen on plastic deformation with the emphasis on the appropriate parameterization of the influence of hydrogen.

Experimental observations in many silicates including quartz, olivine and pyroxenes indicate that plastic deformation due to dislocations is enhanced by the presence of hydrogen. In all cases so far studied, the degree of weakening is positively correlated with the amount of dissolved hydrogen in a given mineral. Also the degree of weakening is correlated with the silica content: the higher the silica content, the more is the weakening by hydrogen. In quartz, this effect is very strong, whereas the weakening effect is modest in olivine.

A generic equation for the rate of deformation by dislocation motion is,

$$\dot{\varepsilon} = \rho b v = \rho b^2 n_i v_i, \tag{19}$$

where $\dot{\varepsilon}$ is strain-rate, ρ is dislocation density, v is dislocation velocity, n_i is the concentration (number per unit length) of "steps" (kinks or jogs) and v_i is their mobility. In writing this equation, we have taken into account the fact that dislocation motion occurs in a step-wise fashion through the motion of individual "steps" such as kinks or jogs. Therefore the dependence of the rate of deformation on hydrogen at steady state[5] can be written as

$$\dot{\varepsilon}(C_w) = \rho b^2 n_i(C_w)\, v_i(C_w)\,. \tag{20}$$

Let us first discuss the dislocation velocity, $v_i(C_w)$. The physical mechanisms that may control the dislocation velocity (mobility) depend on (i) the nature of chemical bonding, (ii) crystal structure, and (iii) the concentration of impurity atoms or secondary phase particles. In most of the silicate minerals or oxides, the nature of chemical bonding is between ionic to covalent. The Si-O is strongly covalent (particularly when it is coordinated with four oxygen ions), whereas Mg-O bond is more ionic. Consequently, the resistance to break chemical bonds is stronger in minerals with high SiO_2 content. In these materials, high-temperature steady-state deformation is controlled, in most cases, either by dislocation climb that is in turn controlled by the diffusion of the slowest moving atomic species or the glide motion of dislocations through the nucleation and migration of double-kinks. In these cases, hydrogen may affect dislocation velocity through two different effects: (i) through the enhancement of the diffusion of the slowest diffusing species, or (ii) through the enhancement of the dislocation glide by reducing the energy for nucleation and/or the migration of kinks.

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[5] The influence of the non-steady-state deformation is important in minerals with strong covalent bonding (e.g., quartz). In these minerals, the creep strength observed in laboratory experiments is largely controlled by dislocation generation, i.e., $\rho\,(C_w, t)$.

A few words need to be added about the density of steps, $n_i(C_w)$. In a material in which the chemical bonding is strong, the density of jogs or kinks is often controlled by thermal equilibrium. In these cases, the density of these steps depends strongly on the energy of the formation of these steps and the chemical environment. The dependence of the density of these steps on chemical environment can be analyzed by considering the following the chemical reaction, where a dislocation line reacts with some chemically active species such as electron holes or water (hydrogen), viz.,

$$h^{\mathrm{g}},\ \mathrm{H_2O} + \textit{dislocation} \Leftrightarrow \textit{charged or hydrated kinks (jogs)}. \tag{21}$$

For this model, the law of mass action gives

$$n_i(C_w) \propto \left[h^{\mathrm{g}}(C_w)\right]\exp\left(-\frac{\Delta G_i\,(C_w,\sigma)}{RT}\right)\ \textit{or}\ \ [\mathrm{H_2O}]\exp\left(-\frac{\Delta G_i\,(C_w,\sigma)}{RT}\right), \tag{22}$$

where $\Delta G_i(\sigma, C_w)$ is the formation free energy of a step. Heggie and Jones (1986) showed that the energy of the formation and migration of kinks on the dislocation line in quartz is reduced by hydrogen; and hence the kink density (and mobility) will be higher at hydrogen-rich conditions.

Experimental observations supporting both cases have been reported. For olivine polycrystals deformed in the dislocation creep regime at high temperatures and low stresses, the experimental observations can be interpreted by the dislocation climb-controlled model (Fig. 6),

$$\dot{\varepsilon}_{\mathrm{wet}} \propto n_i(C_w)\, v_i(C_w) \propto \left[h^{\mathrm{g}}\right] D \propto \left[h^{\mathrm{g}}\right]\left[\mathrm{Si}_I^{\mathrm{gggg}}\right] \propto f_{\mathrm{H_2O}}^{\frac{5}{4}}, \tag{23}$$

where D is diffusion coefficient (Karato and Jung, 2003; Mei and Kohlstedt, 2000b). Therefore the net strain-rate in this case is given by

$$\dot{\varepsilon} = \dot{\varepsilon}_{\mathrm{dry}} + \dot{\varepsilon}_{\mathrm{wet}}, \tag{24}$$

with

$$\dot{\varepsilon}_{\mathrm{wet}} = A \cdot f_{\mathrm{H_2O}}^{\frac{5}{4}} \propto C_w^{\frac{5}{4}}. \tag{25}$$

This interpretation is not unique, however. Other models such as $\dot{\varepsilon} \propto [(3\mathrm{H})'_{Si}]$ can also explain the observed dependence on water fugacity. Additional observations such as the dependence of strain-rate on oxide activity and on oxygen fugacity need to be used to better constrain the model.

For quartz in which the chemical bonding is a strong covalent bond, and Griggs (1974) proposed that creep is controlled by dislocation glide and that hydrogen reduces the energy for nucleation (and growth) of kinks on dislocation line thereby enhances the dislocation glide mobility. Such a model will also apply to other minerals such as olivine at relatively low temperatures and/or high stresses. In this case, the

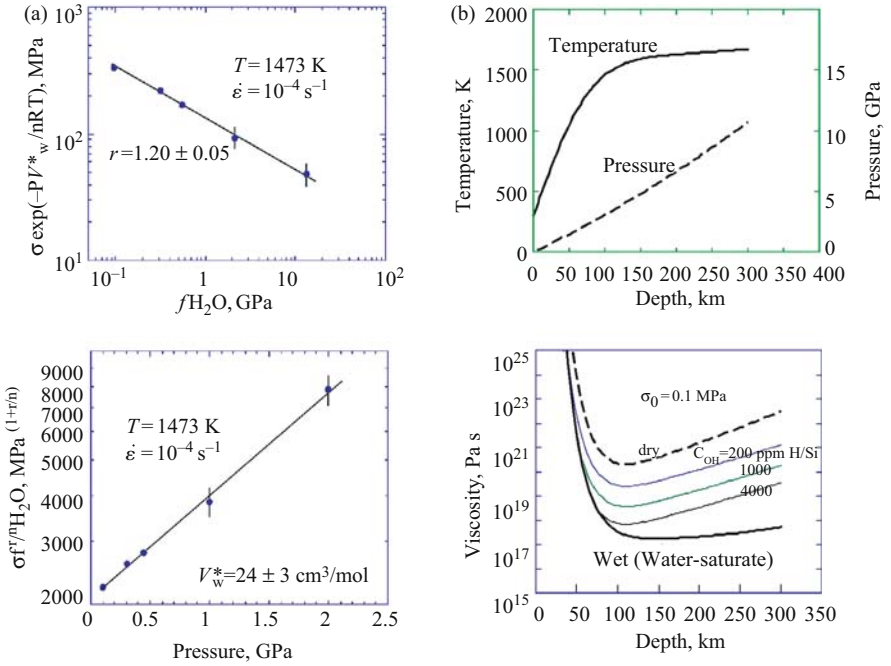


Figure 6. The effects of pressure on dislocation creep in olivine for water (hydrogen)-saturated conditions (after Karato and Jung, 2003). (a) The creep strength can be analyzed using two parameters, r and V^* (ΔV^*), using the relationship, $\dot{\varepsilon} = A\sigma^n f_{H_2O}^r \exp(-PV^*/RT)$. (b) The depth variation of viscosity (for a constant stress) in the upper mantle for a range of water content (bottom) together with the assumed geotherm corresponding to the oceanic environment (age = 100 my) and the pressure-depth relationship (top).

creep rate is proportional to the density of kinks and their mobility and hence (using Eq. (22)),

$$\dot{\varepsilon}_{\text{wet}} \propto [H_2O] \exp\left(-\frac{\Delta G_w(\sigma)}{RT}\right) \propto C_w \exp\left(-\frac{\Delta G_w(\sigma)}{RT}\right), \tag{26}$$

where ΔG_w is the free energy for nucleation and migration of a hydrated double kink. This form of flow law best explains the experimental observations on olivine at relatively high stress levels (Katayama and Karato, 2006a).

So far I have reviewed the influence of hydrogen on the plastic flow of isotropic mineral aggregates. Dislocation creep occurs by the motion of crystal dislocations. By its very definition, the motion of dislocations is anisotropic. Consequently, the influence of hydrogen can also be anisotropic: hydrogen may enhance deformation by different slip systems in a different way. In such a case, the addition of hydrogen will change the relative contribution from different slip systems to the total strain,

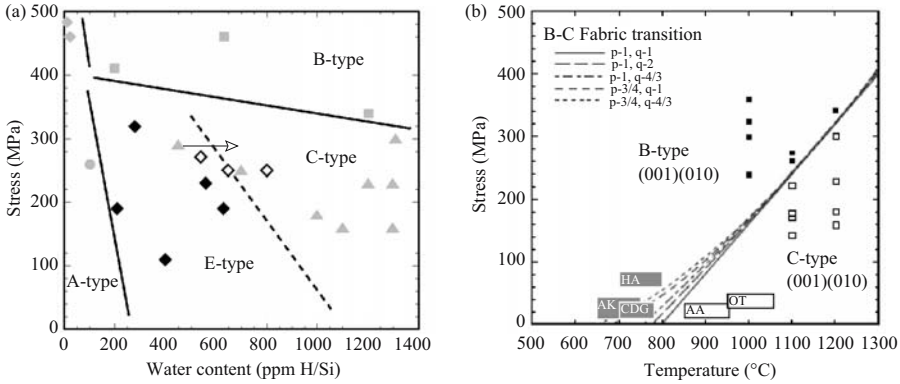


Figure 7. Fabric diagrams for olivine (a) on a stress-water content space at $T \sim 1500$ K (Katayama et al., 2004) and (b) on a stress-temperature space at $C_w \sim 1000$ ppmH/Si (Katayama and Karato, 2006b).

leading to fabric transitions. Hydrogen-induced fabric transitions in olivine was predicted by Karato (1995) and systematically studied by Jung and Karato (2001b), Jung et al. (2006), Karato (1995), Katayama et al. (2004), and Katayama and Karato (2006b) (Fig. 7).

When a fabric transition occurs at relatively low temperatures, the flow laws are best described by an exponential form, i.e., Equation (26). In such a case, the activation free energy for deformation is stress dependent, and in the simplest case, the activation enthalpy, $\Delta H (\Delta G = \Delta H - T\Delta S)$, can be written as

$$\Delta H = \Delta H^o - B\sigma, \tag{27}$$

where ΔH^o is the activation enthalpy at zero stress and B is a constant both of which depend on the slip system. In such a case, the condition for a fabric transition is given by equating the strain-rate for two slip systems as

$$A_1 \exp\left(-\frac{\Delta H_1^o - B_1\sigma}{RT}\right) = A_2 \exp\left(-\frac{\Delta H_2^o - B_2\sigma}{RT}\right). \tag{28}$$

Therefore the fabric boundary is given by

$$RT \log \frac{A_1}{A_2} = \left(\Delta H_1^o - \Delta H_2^o\right) - (B_1 - B_2)\,\sigma. \tag{29}$$

The fabric boundary defined by this equation is insensitive to hydrogen content (as far as a small amount of hydrogen is present), but is sensitive to stress and temperature. This is consistent with the observed fabric transitions from B-type to C-, E-type fabrics (Fig. 7a). This relation is used to extrapolate the experimental data to lower temperatures (the B- to C-type transition) and the results are compared with the

observations on naturally deformed rocks (Fig. 7b). The comparison supports this scaling law.

In contrast, when a fabric transition occurs at high temperature/low stress conditions, then the power-law flow law will apply and then the conditions for a fabric transition will be

$$RT \log \frac{C_1 + D_1 f_{\mathrm{H_2O}}}{C_2 + D_2 f_{\mathrm{H_2O}}} = \Delta H_1^o - \Delta H_2^o. \tag{30}$$

The fabric boundary for this case is controlled essentially by temperature and water fugacity and not by stress. The fabric boundaries between A- and E-type, and between E- and C-type belong to this category (Fig. 7a).

The recognition that hydrogen plays an important role in deformation fabrics has provided a new horizon in interpreting deformation fabrics and seismic anisotropy in terms of flow geometry. In particular, with these new results, the deformation fabrics of rocks from the convergent boundaries and the pattern of seismic anisotropy in these regions can be explained in this model by the regional variation in physical/chemical factors (temperature, water content) rather than the complicated flow patterns (Karato, 2003).

4.3 Grain-boundaries

Hydrogen also affects grain-boundary-related processes. Firstly, grain-boundaries dissolve a higher concentration of hydrogen than the bulk of crystals. Karato et al. (1986) and Mei and Kohlstedt (2000a) noted that fine-grained polycrystalline olivine samples have a larger amount of dissolved hydrogen than their single crystal counterpart. Jung and Karato (2001a) reported that the size of dynamically recrystallized grains in olivine is larger in hydrogen-rich conditions compared to hydrogen-poor conditions. They concluded that this is due to the larger extent of the enhancement of grain-boundary mobility than dislocation mobility using a theory for dynamically recrystallized grain-size by Derby and Ashby (1987). Similarly, Nishihara et al. (2006) found that grain-growth kinetics in wadsleyite is enhanced by hydrogen as (Fig. 8)

$$k = k_{\mathrm{dry}} + k_{\mathrm{wet}}, \tag{31}$$

with

$$k_{\mathrm{wet}} \propto f_{\mathrm{H_2O}}^q \propto C_w^q, \tag{32}$$

with $q \sim 2$ and $L^n - L_0^n = k\,(T, P, C_w)\,t$ (L: grain-size, and t: time). In all cases so far studied, hydrogen enhances grain-boundary processes more than intra-granular processes. Nishihara et al. (2006) suggested that this may be due to the influence of hydrogen not only on diffusion coefficients but also on some grain-boundary properties such as the density of ledges and/or grain-boundary width. Material transport

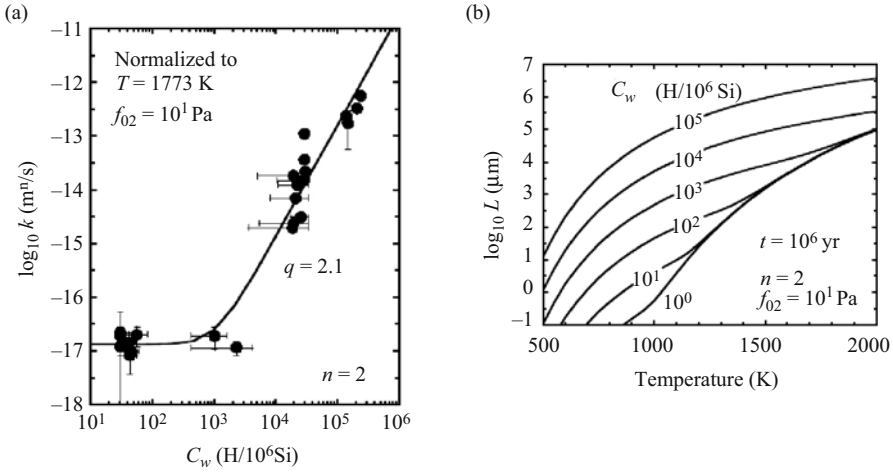


Figure 8. Influence of hydrogen on the rate of grain-growth in wadsleyite (after Nishihara et al., (2006)). (a) The kinetic constant, k, for grain-growth as a function of water content. A constant $k$is defined by $L^n - L_0^n = k\,(T, P, C_w)\,t$ (L: grain-size, L_0: initial grain-size, and t: time). Grain-growth kinetics in wadsleyite shows much stronger dependence on hydrogen content than other properties such as electrical conductivity and diffusion. (b) The grain-size due to grain-growth as a function of annealing temperature and water content. Initial grain-size is assumed to be much smaller than the final grain-size ($L = t^{1/n} k(T, P, C_w)^{1/n}, P = 16$ GPa). A small grain-size, $L < 100$ μm, can be maintained for 1 my only in relatively hydrogen-free and/or low temperature conditions.

across a grain-boundary involves formation of grain-boundary steps "ledges" and migration of steps by diffusion. The density of ledges may increase with water fugacity if the density of ledges is controlled by a reaction similar to (21). Grain-boundary sliding involves formation and migration of ledges and therefore also likely depends strongly on hydrogen content. Strong dependence of grain-growth kinetics on hydrogen content implies that the grain-size in and hence the strength of subducting slabs after the olivine-wadsleyite (or olivine-ringwoodite) phase transformation is likely dependent on hydrogen content as well as on temperature. A small grain-size can be maintained only at relatively hydrogen-free and/or low temperature environment.

5 SOME APPLICATIONS

5.1 Influence of hydrogen on plastic deformation in deep mantle minerals

The Earth's mantle is ∼3000 km thick and plastic deformation in this thick mantle controls the evolution of this planet. One of the most challenging issues in studying the influence of hydrogen on rheological properties is to conduct experimental studies under deep Earth conditions. I have shown that even for the upper mantle minerals it is critical to conduct quantitative deformation experiments above ∼2 GPa in order to

obtain any meaningful data that can be extrapolated to the Earth's interior below a few 10s of km. Although a gas apparatus such as the one developed by Paterson (1990) provides a high resolution mechanical data and has been used in many laboratories (e.g., Mei and Kohlstedt, 2000a; Mei and Kohlstedt, 2000b), the maximum pressure of operation of that apparatus is ∼0.5 GPa. The data obtained under these conditions cannot be used to infer the rheological properties of majority of Earth's mantle.

Currently Karato and Jung (2003) is the only paper in which all the parameters needed for extrapolation to the Earth's deep mantle are determined for olivine (for dislocation creep regime) under controlled hydrogen content. Their experimental studies were conducted to 2.2 GPa (water fugacity ∼13 GPa) and the deviatoric stress was determined using a dislocation density-stress calibration curve. Quantitative experimental studies beyond this pressure range are limited. Two types of high pressure deformation apparatus have been developed: D-DIA (deformation DIA) (Wang et al., 2003) and RDA (rotational Drickamer apparatus) (Xu et al., 2005; Yamazaki and Karato, 2001a). In both cases, controlled deformation of a sample is possible under high pressure and temperature conditions, and the rheological measurements can be performed using a synchrotron X-ray facility. To date, D-DIA has been operated to ∼10 GPa and ∼1600 K (e.g., Li et al., 2004) and RDA has been operated to ∼16 GPa and ∼1800 K (Nishihara et al., 2005). However, quantitative experiments on rheological properties under controlled hydrogen content (water fugacity) have not been performed under these conditions.

Consequently, the influence of hydrogen on rheological properties of minerals in the deep mantle is not well constrained at this time. However, for wadsleyite, we now have a good idea about the atomistic mechanisms of hydrogen dissolution including the nature of charged defects. Processes related to point defects (such as electrical conductivity) in wadsleyite (and ringwoodite) are enhanced by the dissolution of hydrogen. Grain-growth kinetics involving grain-boundary processes in wadsleyite is enhanced by hydrogen. Therefore it is almost certain that plastic deformation in wadsleyite and ringwoodite (either by diffusion of point defects or by dislocation motion) is enhanced by hydrogen. Indirect evidence is available suggesting the enhancement of dislocation motion by hydrogen in wadsleyite (e.g., Kubo et al., 1998). However, there have not been any quantitative experimental studies on the influence of hydrogen on plastic deformation of wadsleyite. Quantitative studies on plastic deformation in wadsleyite (and other deep mantle minerals) are underway in my laboratory. Our preliminary results show a high strength of wadsleyite at water-poor conditions and weakening effects by hydrogen (Nishihara et al., 2005).

Much less is known about the influence of hydrogen in lower mantle minerals. For (Mg,Fe)O, the dominant hydrogen-related defect is either H'_M or $(2H)^{\times}_M$. Deformation of this material occurs either by diffusion of point defects or by dislocation motion, but deformation by dislocation motion is also controlled by diffusion of point defects (kink formation and migration and jog formation are easy in this material because of a small Peierls stress due to weak chemical bonding). Consequently, the influence of hydrogen on deformation of this material can be understood from the results given in Figure 4 the results in Fig. 4 can be applied to (Mg,Fe)O ignoring the defects associated

with Si as far as the charge neutrality condition under hydrogen-rich condition is $[H'_M] = [Fe^g_M]$). In evaluating the influence of hydrogen on deformation in (Mg,Fe)O, I include the following notions: (i) in (Mg,Fe)O, dislocation creep is controlled by dislocation climb that is controlled by diffusion of oxygen. Diffusion of oxygen in (Mg,Fe)O occurs through the diffusion of oxygen vacancies or the diffusion of a neutral defect pair $V''_M - V^{gg}_O$ (see e.g., Ando, 1989). In the former case, the rate of deformation is proportional to $f^{1/2}_{H_2O}$, whereas in the latter, it is insensitive to hydrogen content ($[V''_M - V^{gg}_O] \propto f^0_{H_2O}$). In either case, the influence of hydrogen on plastic deformation by dislocation creep is likely weaker for (Mg,Fe)O than olivine or other silicates. (ii) Diffusion creep in (Mg,Fe)O may be rate-controlled by the volume diffusion of oxygen or by the volume diffusion of Mg (Fe). The latter occurs due to the selected enhancement of oxygen diffusion along grain-boundaries, making the total effective diffusion coefficient of Mg less than that of oxygen (Gordon, 1973). In this case, the creep rate will be proportional to f_{H_2O} (C_w) if $(2H)^\times_M$ is the dominant defect. If one accepts the best documented notion that the volume diffusion of oxygen in (Mg,Fe)O occurs through the diffusion of $V''_M - V^{gg}_O$ and the diffusion creep is rate-controlled by the volume diffusion of Mg (Fe), then the conclusions on the hydrogen effects are (i) hydrogen has no effects on dislocation creep in (Mg,Fe)O, but (ii) hydrogen has effects similar to olivine for diffusion creep (i.e., $\dot{\varepsilon} \propto f_{H_2O}$).

What about silicate perovskites? Virtually nothing is known on the influence of hydrogen on physical properties of silicate perovskites. However, based on the Mössbauer spectroscopy, the dominant point defects in an Al-containing $(Mg,Fe)SiO_3$ perovskite are known to be Al'_{Si} and Fe^g_M (McCammon, 1997). The chemical reaction associated with these defects is

$$\frac{1}{2}Al_2O_3 + \frac{1}{4}O_2 + Fe^\times_M + Si^\times_{Si} \Leftrightarrow Al'_{Si} + Fe^g_M + SiO_2. \tag{33}$$

If the two defects Al'_{Si} and Fe^g_M are the dominant charged defects, then (note that the activity of SiO_2 is fixed by the co-existence of perovskite and magnesiowüsitite)

$$\left[Al'_{Si}\right] = \left[Fe^g_M\right] \propto f^{\frac{1}{8}}_{O_2} a^{\frac{1}{4}}_{Al_2O_3}. \tag{34}$$

The concentrations of these defects are large (more than 10% ; e.g., McCammon, 1997) and hydrogen solubility in perovskite is small (∼10 ppmH/Si or less; e.g., Bolfan-Casanova et al., 2000[6]). Consequently, the incorporation of hydrogen will not change the concentrations of defects at sites other than the one in which hydrogen is incorporated. If analogy with other silicates is a guide, the likely sites at which hydrogen is dissolved in $(Mg,Fe)SiO_3$ perovskite will be either M- or Si-sites (i.e., $(2H)^\times_M$ or $(4H)^\times_{Si}$). Therefore using the model developed in section 4.1 (the results

[6] A much higher "water" solubility was reported by Murakami et al. (2002), but this report is likely in error, because much of the absorption peaks occur at ∼3400 cm^{-1} corresponding to water in fluids or glassy phases. It is likely that their samples contain a number of fluid phase inclusions.

of Fig. 4 can be applied to (Mg,Fe)SiO_3), I conclude that the rate of deformation will be related to water fugacity as $\dot{\varepsilon} - \dot{\varepsilon}_{\rm dry} \propto f_{H_2O}^q \propto C_w^q$ with $q = 1$ if the defects at M-site control the rate of deformation and $q = 2$ if the defects at Si-site control the rate of deformation. In these cases, the influence of hydrogen will be large if plastic deformation under dry conditions is very difficult. The degree to which hydrogen enhances deformation in these cases is primarily controlled by the ratio of the concentration of the point defects at these sites under dry conditions to the concentration of hydrogen-related defects. Judging from the high solubility of trace elements in $CaSiO_3$ perovskite (Corgne and Wood, 2002; Hirose et al., 2004), it is likely that a very small amount of hydrogen (less than 1 ppm H/Si) goes to (Mg,Fe)SiO_3 perovskite in the Earth's lower mantle (a case analogous to hydrogen depletion by partial melting proposed by Karato (1986)). Therefore the influence of hydrogen on plastic deformation in (Mg,Fe)SiO_3 perovskite is likely not very large, unless the concentration of defects under dry conditions is significantly smaller than ~1 ppm.

In evaluating the role of hydrogen in the plastic deformation of the lower mantle phases, it is important to estimate the partitioning of hydrogen as well as the magnitude of hydrogen effect in each phase. The partitioning of hydrogen can be estimated from the experimental results of Bolfan-Casanova et al. (2000) and Bolfan-Casanova et al. (2002), suggesting that more hydrogen is dissolved in (Mg,Fe)O than (Mg,Fe)SiO_3 perovskite. However, I note that Bolfan-Casanova et al. (2002) probably underestimated the hydrogen solubility in (Mg,Fe)O due to the effect of unquenchable hydrogen in their samples.[7] Therefore I conclude that the true partitioning coefficient of hydrogen between (Mg,Fe)O and (Mg,Fe)SiO_3 perovskite is yet to be determined (more hydrogen is likely dissolved in (Mg,Fe)O than was concluded by Bolfan-Casanova et al. (2002). Obviously a lot more research is needed in this area.

5.2 Influence of hydrogen on seismic wave velocities and attenuation

The mechanisms by which hydrogen might influence the seismic wave propagation can be classified into three categories: (i) the addition of hydrogen changes elastic constants due to weak chemical bonding and hence reduces seismic wave velocities, (ii) the addition of hydrogen enhances anelastic relaxation and hence reduces seismic wave velocities and (iii) hydrogen may also modify the relative strength of slip systems and could change the lattice-preferred orientation which changes seismic anisotropy (see Karato, 1995). The third topic is discussed in Section 4.2, so I will briefly review first two topics here assuming elastic isotropy.

[7] The infrared absorption spectra reported by these authors include absorption peaks due to $Mg(OH)_2$ and free water. (Bolfan-Casanova et al., 2002) ignored the hydrogen content associated with these peaks in calculating the hydrogen solubility, but these absorption peaks likely correspond to the hydrogen dissolved in the (Mg,Fe)O lattice at high temperature and pressure that was not quenched. If this is true the actual solubility is ~5–10 times more than the values that they reported.

The basic point is that seismic wave velocities can be modified by hydrogen by two different mechanisms. First is the change in seismic wave velocities through the change in density and (high-frequency) elastic moduli and second is the change in seismic wave velocities through the enhanced attenuation. The direct effect of hydrogen on elasticity was studied using high-frequency elasticity measurements on hydrogen-bearing minerals such as hydrous wadsleyite or hydrous ringwoodite (Inoue et al., 1998; Jacobsen et al., 2004; Yusa and Inoue, 1997[8]). There are some differences in the experimental results particularly on the shear modulus. However, all studies show ∼2–3% reduction in high-frequency seismic wave velocities for 1 wt% addition of water. I conclude that the effects of hydrogen on high-frequency seismic wave velocities could be significant only at relatively high hydrogen content (∼1 wt% water or more). At a smaller hydrogen content (0.1 wt% water or less), this direct influence is less than 0.2–0.3% and consequently, does not play an important role.

How about the indirect influence through anlasticity? (Jackson et al., 1992) conducted the first systematic measurements of seismic wave attenuation under confining pressure. Under their experimental conditions ($T < 1500$ K, $P = 0.3$ GPa), the fugacity of water was ∼0.3 GPa. They observed appreciably higher seismic wave attenuation in samples (dunite, i.e., olivine-dominated polycrystals) that contain more hydrogen than samples from which most of the hydrogen had been removed by heat treatment prior to the experiments. Since many complications occurred in their samples in this pioneering study using a natural dunite, they did not conclude that the difference in attenuation between the two types of sample is due to the difference in hydrogen content. However, in view of our current knowledge on the influence of hydrogen on defect-related properties, this observation is most likely the results of change in hydrogen content in olivine.

A brief theoretical analysis is given below to support the plausibility of this interpretation. First note that seismic wave attenuation under high-temperature, low-frequency regimes obeys the following power-law relationship,

$$Q^{-1}(\omega, T, P, C_w) \propto \omega^{-\alpha}, \tag{35}$$

where ω is the frequency, and α is a constant (∼0.2–0.4). From the dimensional analysis, this implies $Q^{-1}(\omega, T, P, C_w) \propto [\omega \cdot \tau(T, P, C_w)]^{-\alpha}$ where $\tau(T, P, C_w)$ is the relaxation time that depends on the rate of viscous processes involved (T: temperature, P: pressure, C_w: hydrogen content). In most mechanisms of high-temperature attenuation, viscous processes involved in attenuation are similar to long-term creep (Jackson et al., 2000; Karato and Spetzler, 1990), although details can be different. Consequently, $Q^{-1}(\omega, T, P, C_w) \propto \dot{\varepsilon}\,(T, P, C_w)^{\alpha}$ and therefore $Q^{-1}(\omega, T, P, \text{wet})/Q^{-1}(\omega, T, P, \text{dry}) = [\dot{\varepsilon}\,(T, P, \text{wet})/\dot{\varepsilon}\,(T, P, \text{dry})]^{\alpha}$. Alternatively, the relaxation time may be related to the characteristic time for

[8] (Jacobsen et al., 2004)'s results include the influence of Fe/(Fe+Mg) ratio, and the intrinsic effects of hydrogen is smaller than they reported if the effect of Fe/(Fe+Mg) ratio is corrected.

grain-boundary sliding. In this case, $Q^{-1}(\omega, T, P, \text{wet})/Q^{-1}(\omega, T, P, \text{dry}) = [v\,(T, P, \text{wet})/v\,(T, P, \text{dry})]^{\alpha}$ where v is the velocity of grain-boundary sliding (I used a relation $\tau \approx L/v$ with L: grain-size and v: velocity of grain-boundary sliding, and assumed that grain-size did not change with hydrogen content in these experiments). Both dislocation creep and diffusional creep, and all grain-boundary related processes in olivine are known to be enhanced by the dissolution of hydrogen (see previous sections). Therefore it would be surprising if attenuation is *not* enhanced by hydrogen. In the case of (Jackson et al., 1992), the results can be directly compared with the results of (Chopra and Paterson, 1984) who studied the plastic deformation of the exactly same dunite at nearly identical conditions. The results of these studies satisfy the relation $Q^{-1}(\omega, T, P, \text{wet})/Q^{-1}(\omega, T, P, \text{dry}) = [\dot{\varepsilon}\,(T, P, \text{wet})/\dot{\varepsilon}\,(T, P, \text{dry})]^{\alpha}$ reasonably well ($Q^{-1}(\text{wet})/Q^{-1}(\text{dry}) \approx 2$ and $\dot{\varepsilon}\,(\text{wet})/\dot{\varepsilon}\,(\text{dry}) \approx 10$ and hence $Q^{-1}(\omega, T, P, \text{wet})/Q^{-1}(\omega, T, P, \text{dry}) = [\dot{\varepsilon}\,(T, P, \text{wet})/\dot{\varepsilon}\,(T, P, \text{dry})]^{\alpha}$ with $\alpha = 0.3$). Therefore I conclude that the influence of hydrogen (water) on seismic wave attenuation is as well established as the influence of hydrogen on plastic deformation by the study of Chopra and Paterson (1984). A major uncertainty includes the possible influence of grain-boundary sliding. The deformation experiments by Chopra and Paterson (1984) investigated the influence of hydrogen on dislocation creep. Seismic wave attenuation may be due either to dislocation motion or to grain-boundary sliding (Jackson et al., 2000; Karato and Spetzler, 1990). If grain-boundary sliding is important, then a comparison such as $Q^{-1}(\omega, T, P, \text{wet})/Q^{-1}(\omega, T, P, \text{dry}) = [\dot{\varepsilon}\,(T, P, \text{wet})/\dot{\varepsilon}\,(T, P, \text{dry})]^{\alpha}$ is not appropriate if strain-rates are for dislocation creep; and the influence of hydrogen on attenuation will be more important than the case of dislocation-related mechanism.

Combining (31) with an equation for high-frequency, unrelaxed velocity, I get

$$v\,(\omega, T, P, C_w) = v_{\infty}\,(T, P, C_w)\left[1 - \frac{1}{2}\cot\frac{\pi\alpha}{2}Q^{-1}\,(\omega, T, P, C_w)\right], \tag{36}$$

with

$$v_{\infty}\,(T, P, C_w) = \bar{v}_{\infty}\,(P)\,[1 - A\,(P)\,T]\,[1 - B\,(P)\,C_w], \tag{37}$$

and

$$Q^{-1}\,(\omega, T, P, C_w) \propto C_w^{\alpha q}, \tag{38}$$

where $\tau \propto C_w^{-q}$ with $q = 1 - 2$ (1 for dislocation mechanism, 2 for grain-boundary mechanism) and $A\,(P)$ and $B\,(P)$ are constants. This formulation was used in inverting the results of seismic tomography by Shito et al. (2006).

The frequency dependence of seismic wave attenuation in the lower mantle is similar to that in the upper mantle (Shito et al., 2004; Smith and Dahlen, 1981), therefore the sensitivity of attenuation to the relaxation time should be similar between two regions. Assuming a similar functional dependence of attenuation on hydrogen content in the transition zone and the lower mantle minerals, the influence of hydrogen on seismic wave attenuation and velocity in these regions is expected to be large. Figure 9

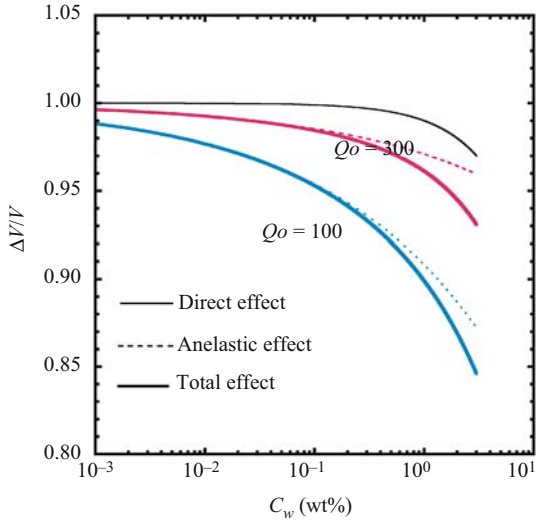


Figure 9. The influence of hydrogen on seismic wave velocities. $\Delta V/V$ is the fraction of velocity variation due to the addition of hydrogen, and C_W is the hydrogen content (wt% water). Qo is the background Q (background Q in the upper mantle is ∼100, whereas in the transition zone and the lower mantle it is ∼300 (in the PREM). A direct effect through the effects on unrelaxed velocity plays a lesser role than anelasticity in most regions of the Earth's mantle, except in regions with very large water content. The hydrogen content exponent is assumed to be $q = 1$.

compares the influence of hydrogen on seismic wave velocities through its effects on unrelaxed velocity (direct effect) and through anelasticity. The data on $B(P)$ are from Inoue et al. (1998), Jacobsen et al. (2004), and Yusa and Inoue (1997), and $\alpha = 0.3$ (e.g., Shito et al., 2004; Smith and Dahlen, 1981) and $q = 1$ are used. I conclude that the hydrogen affects seismic wave velocities mainly through anelasticity in the upper mantle where the background Q is low (∼100). In the transition zone (where the background Q is ∼300), the influence of hydrogen through unrelaxed velocity will be important if the hydrogen content exceeds ∼1 wt% equivalent of water. For hydrogen content less than 0.1 wt% water, the influence through anelasticity is more important. In the lower mantle, because the solubility of hydrogen is so low, a direct effect through unrelaxed velocity is almost definitely unimportant, and the effects through anelasticity would be important if a significantly large variation in hydrogen content (say, ∼0.1 wt% water) is present.

5.3 Some speculations on the role of hydrogen on geodynamic processes and plume structures

Hydrogen can have dramatic effects on the evolution and dynamics of terrestrial planets through its influence on melting temperature and rheological properties. The influence of hydrogen on physical properties on olivine has been studied extensively.

The importance of redistribution of hydrogen by partial melting in the shallow upper mantle has been discussed by Hirth and Kohlstedt (1996), Karato (1986), and Korenaga (2003). In particular, Korenaga (2003) pointed out the importance of shallow mantle dynamics for the evolution of the whole of the Earth because of the large energy dissipation in that region. However, the validity of this model is uncertain because the contribution to energy dissipation from deep mantle deformation is currently poorly constrained. Quantitative studies on hydrogen-related defects and their influence on physical (and chemical) properties (especially rheological properties) in deep Earth minerals are critical in order to advance our knowledge on the dynamics and evolution of terrestrial planets. Here I will review the current knowledge of the role of hydrogen in minerals in the deep interior of the mantle.

One important concept that comes from the atomistic model of hydrogen-related defects in minerals (see Section 5.1) is that in the upper mantle and the transition zone, hydrogen is likely to be dissolved in major minerals (olivine, orthopyroxene, wadsleyite, ringwoodite, and majorite) that control the rheological properties in these regions. In the lower mantle, however, hydrogen is likely in a minor phase, $CaSiO_3$ perovskite, that does not have direct influence on the rheological properties of this region (because of a very small volume fraction, less than $\sim$5%). The amount of $CaSiO_3$ perovskite (i.e., the Ca content) is controlled by the previous history of this region: regions that contain a large amount of materials of paleo-oceanic crust will have a higher content of $CaSiO_3$ perovskite and if dehydration during subduction process is imperfect, this region will have high hydrogen content. Consequently, regions with a high content of $CaSiO_3$ perovskite generally have higher hydrogen content in major minerals as well, and hence are prone to gravitational instability causing plumes due to a reduced viscosity. Plumes coming from these regions will have a higher content of elements that are enriched in the oceanic crust (Ca, Al, Fe). Nolet et al. (2005) suggested Fe-enrichment for plumes based on a plume-flux argument using the results of high-resolution tomographic imaging.

The transition zone minerals such as wadsleyite and ringwoodite can store a large amount of hydrogen. Based on a simple material circulation model, Richard et al. (2002) argued that the transition zone of the Earth might have little water due to the effective removal of hydrogen. However, Bercovici and Karato (2003) suggested that the melting caused by dehydration in an upwelling flow at 410-km could dramatically modify the distribution of hydrogen and other trace elements. In this model, hydrogen (and other trace elements) could be sequestered in the deep mantle through their dissolution in a dense hydrous melt and subsequent transfer to the deep mantle. However, the details of processes of hydrogen transfer in the deep mantle are poorly understood at this time.

Materials transport in the deep mantle occurs partly in the form of concentrated upwelling or downwelling, called "plumes". Recently, Montelli et al. (2004) obtained the first high-resolution images of upwelling plumes using a non-linear inversion scheme incorporating the frequency dependence of seismic wave propagation. Nolet et al. (2005) inverted the tomographic images in terms of thermal and chemical anomalies to estimate the amount of heat transport by plumes. By its very nature,

plumes are associated with thermal as well as chemical anomalies, and the issue of distinguishing them is not trivial. Here I will provide a brief discussion about the possible role of hydrogen on plume structure.

One of the remarkable observations on plumes seen through seismic tomography is that plumes are rather thick and not so hot (Montelli et al., 2004; Nolet et al., 2005). A direct conclusion from the observed thick plume is that the viscosity of plume materials is not much smaller than the viscosity of surrounding materials (Karato, 2000). Let us consider how hydrogen might influence the rheological properties and seismological signatures of plumes.

Since the most robust tomographic imaging is from the lower mantle, I will focus on the lower mantle. Karato et al. (1995) showed that most of the lower mantle deforms by diffusion creep. In such a case, the viscosity of a material strongly depends on the grain-size. Now, in the diffusion creep regime, grain-size is controlled by grain-growth kinetics. Consequently, grain-size will depend on temperature and hydrogen content. We may distinguish two cases: Case I in which the time scale of grain-growth is much larger than the time scale of relevant deformation. In such a case, grain-size can be regarded as a constant and independent of temperature and hydrogen content. Case II is a case in which the time constant of grain-growth is comparable to or smaller than that of deformation. In such a case, temperature and hydrogen content dependence of grain-size must be considered.

Following the suggestion by Solomatov (1996), Korenaga (2005) assumed case II behavior and proposed that the viscosity of plume (source region at least) may have positive correlation with temperature. This notion comes from the fact that once one assumes diffusion creep, then the viscosity depends on grain-size, L, and diffusion coefficient, D, as $\eta(T) \propto L(T)^m D(T)^{-1}$ and hence if grain-size is controlled by grain-growth kinetics, then

$$\eta(T) \propto \exp\left(-\frac{\frac{m}{n}H^*_{gg} - H^*_{\text{diff}}}{RT}\right), \tag{39}$$

where $\eta(T)$ is viscosity, m is the grain-size exponent for diffusion creep ($m = 2$–3), n is the grain-growth exponent, H^*_{gg} is the activation enthalpy for grain-growth, and H^*_{diff} is the activation enthalpy for diffusion. If $m/nH^*_{gg} - H^*_{\text{diff}} > 0$, then the viscosity and temperature will have a *positive* correlation. Although currently available experimental data on grain-growth kinetics and diffusion in the lower mantle minerals do not support this inequality (Yamazaki and Irifune, 2003; Yamazaki et al., 1996; Yamazaki et al., 2001), it is possible that this inequality may be met under some conditions.[9]

[9] Yamazaki et al., 1996 reported a rather large n value ($n = 10$–11) for grain-growth. For this large n, and for the reported values of activation enthalpies, $(m/n)H^*_{gg} - H^*_{\text{diff}} < 0$. But the reported unusually high n values may be an artifact due to elastic interactions of grains or the progressive loss of hydrogen during annealing experiments (for a reasonable range of models, $n = 3$–4 is predicted for the Ostwald ripening mechanisms of grain-growth).

What about the influence of hydrogen? There is evidence that a higher amount of hydrogen is present in the plume source regions (e.g., Nichols et al., 2002; Wallace, 1998). Let us distinguish the two cases discussed above. In case I, the influence of hydrogen on viscosity is simply through diffusion. If viscosity is controlled by that of (Mg,Fe)O by diffusion creep (Yamazaki and Karato, 2001b) and if the bulk diffusion of Mg (Fe) rate-controls the deformation, then we expect $\eta \propto C_w^{-1}$ (see Section 5.1). And hydrogen will also enhance seismic wave attenuation, $Q^{-1} \propto C_w^{\alpha r}$ and hence reduce the seismic wave velocities (see Section 5.2) (α: frequency exponent of Q, r: a hydrogen content exponent for grain-boundary sliding).

Let us now consider a case II where grain-size is controlled by grain-growth kinetics. Using the previous discussions on the influence of hydrogen on viscosity and attenuation, I get the following equations for the influence of hydrogen on these properties,

$$Q^{-1} \propto \tau^{-\alpha} = \left(\frac{L}{v}\right)^{-\alpha} \propto f_{\mathrm{H_2O}}^{-\alpha\left(\frac{q}{n}-s\right)} \propto C_w^{-\alpha\left(\frac{q}{n}-s\right)}, \tag{40}$$

$$\eta \propto L^m D^{-1} \propto f_{\mathrm{H_2O}}^{\frac{mq}{n}-1} \propto C_w^{\frac{mq}{n}-1}, \tag{41}$$

where α is the exponent for the frequency dependence of attenuation, q is the exponent for hydrogen content dependence of grain-growth kinetics, s is the exponent related to the dependence of grain-boundary sliding rate on hydrogen content and m is the grain-size exponent of diffusional creep. In writing these equations, I have made the following assumptions: (1) Seismic wave attenuation is through grain-boundary sliding (e.g., Jackson et al., 2002), and (2) plastic deformation occurs by diffusion creep (e.g., Karato et al., 1995). If we accept typically observed values of these constants ($\alpha \sim 0.3$, $q \sim 2$, $r \sim 2$, $m \sim 3$, $n \sim 3$), then $Q^{-1} \propto C_w^{0.4}$ and $\eta \propto C_w$. So in this case, a high water content will reduce the seismic wave velocity and increases the viscosity due to the combined effect of increased grain-size and increased relevant diffusion coefficients. In both cases, the addition of hydrogen will increase seismic wave attenuation and hence reduces seismic wave velocities. Inferred high viscosity of plumes may partly be due to a higher hydrogen content. The temperature anomalies, and hence the heat flux carried by plumes, will need to be re-calculated using the corrections for hydrogen effects.

I started this review of the relatively well-established aspect of this area of science, namely the solubility mechanisms of hydrogen in silicate minerals and its influence on phase relationships, and ended up with highly speculative discussions on the plausible role of hydrogen in controlling the rheological properties of deep mantle minerals and seismic wave propagation (attenuation). Here I will list some key mineral physics issues that need to be investigated in the near future:

(i) The solubility of hydrogen in minerals must be better determined.
   a. The theoretical basis for hydrogen content versus infrared absorption (e.g., Paterson, 1982) must be better understood.

b. Intrinsic temperature dependence of hydrogen solubility in wadsleyite (and ringwoodite) must be better determined.
c. Hydrogen solubility in the lower mantle minerals ((Mg,Fe)O, (Mg,Fe)SiO_3 perovskite, $CaSiO_3$ perovskite, a post-perovskite phase) needs to be better determined.

(ii) The influence of hydrogen on melt properties including density and melting relations needs to be investigated under deep mantle conditions. I should point out that melting in the transition zone is highly likely due to the influence of volatile components, but the density of melts thus formed can be lighter or heavier than the surrounding solids depending on the melt composition. The variation of melt density on the composition (particularly the amount of water and potassium) controls the fate of melt. This has an important implication for the volcanic activity of deep origin including plumes (Karato et al., 2006).

(iii) The influence of hydrogen on anelasticity needs to be investigated more systematically.

(iv) The influence of hydrogen on the plastic properties of deep mantle minerals needs to be determined.

(v) The kinetics of grain-growth in a multi-phase system such as a perovskite + magnesiowüstite system needs to be investigated more thoroughly including the effects of hydrogen.

It should be emphasized that most of these experimental studies involve development of new experimental techniques and/or careful experimentation in controlling or characterizing the hydrogen contents. It is also emphasized that the results of these studies must be parameterized in an appropriate way in order to justify their applications to Earth science problems. This requires a sound theoretical understanding of basic physics, particularly the scaling laws for a given property. It is through a combination of these mineral physics studies with observational geophysics/geochemistry and geodynamic modeling that we can make a major progress in revealing the evolution and dynamics of Earth and other terrestrial planets.

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REFERENCES

Akaogi, M., E. Ito, and A. Navrotsky (1989) Olivine-modified spinel-spinel transitions in the system Mg_2SiO_4-Fe_2SiO_4: Calorimetric measurements, thermochemical calculation, and geophysical application. *J. Geophys. Res.*, 94, 15671–15685.

Ando, K. (1989) Self-diffusion in oxides. In Karato, S., and M. Toriumi (eds.) Rheology of Solids and of the Earth, Oxford University Press, pp. 57–82.

Bai, Q., and D.L. Kohlstedt (1993) Effects of chemical environment on the solubility and incorporation mechanism for hydrogen in olivine. *Phys. Chem. Miner.*, 19, 460–471.

Béjina, F., O. Jaoul, and R.C. Liebermann (2003) Diffusion at high pressure: A review. *Phys. Earth Planet. Inter.*, 139, 3–20.

Bell, D.R., G.R. Rossman, J. Maldener, D. Endisch, and F. Rauch (2003) Hydroxide in olivine: A quantitative determination of the absolute amount and calibration of the IR spectrum. *J. Geophys. Res.*, 108, doi: 10.1029/2001JB000679.

Bercovici, D., and S. Karato (2003) Whole mantle convection and transition-zone water filter. *Nature*, 425, 39–44.

Bolfan-Casanova, N., H. Keppler, and D.C. Rubie (2000) Water partitioning between nominally anhydrous minerals in the MgO-SiO_2-H_2O system up to 24 GPa: Implications for the distribution of water in the Earth's mantle. *Earth Planet. Sci. Lett.*, 182, 209–221.

Bolfan-Casanova, N., S.J. Mackwell, H. Keppler, C. McCammon, and D.C. Rubie (2002) Pressure dependence of H solubility in magnesiowüstite up to 25 GPa: Implications for the storage of water in the Earth's lower mantle. *Geophys. Res. Lett.*, 29, 89-1/89-4.

Burnham, C.W. (1979) The importance of volatile constituents. In Yorder J.H.S. (eds.) The Evolution of the Igneous Rocks, Princeton University Press, Princeton, New Jersey, pp. 439–482.

Chen, J., T. Inoue, H. Yurimoto, and D.J. Weidner (2002) Effect of water on olivine-wadsleyite phase boundary in the $(Mg,Fe)_2SiO_4$ system. *Geophys. Res. Lett.*, 29, doi: 10.1029/2001GRL014429.

Chopra, P.N., and M.S. Paterson (1984) The role of water in the deformation of dunite. *J. Geophys. Res.*, 89, 7861–7876.

Cordier, P., J.A. Weil, D.F. Howarth, and J.-C. Doukhan (1994) Influence of the $(4H)_{Si}$ defect on dislocation motion in crystalline quartz. *Eur. J. Mineral.*, 6, 17–22.

Corgne, A., and B.J. Wood (2002) $CaSiO_3$ and $CaTiO_3$ perovskite-melt partitioning of trace elements: Implications for gross mantle differentiation. *Geophys. Res. Lett.*, 29, doi: 10.1029/2001GL014398.

Dasgupta, R., and M.M. Hirschmann (2006) Deep melting in the Earth's upper mantle caused by CO_2. *Nature*, 440, 659–662.

Demouchy, S., E. Deloule, D.J. Frost, and H. Keppler (2005) Pressure and temperature-dependence of water solubility in iron-free wadsleyite. *Am. Mineral.*, 90, 1084–1091.

Derby, B., and M.F. Ashby (1987) On dynamic recrystallization. *Scripta Metallurgica*, 21, 879–884.

Doukhan, J.-C., and M.S. Paterson (1986) Solubility of water in quartz. *Bull. Mineral.*, 109, 193–198.

Gordon, R.S. (1973) Mass transport in the diffusional creep of ionic solids. *Journal of the American Ceramic Society*, 65, 147–152.

Griggs, D.T. (1974) A model of hydrolytic weakening in quartz. *J. Geophys. Res.*, 79, 1653–1661.

Heggie, M., and R. Jones (1986) Models of hydrolytic weakening in quartz. *Philosophical Magazine, A.*, 53, L65–L70.

Hier-Majumder, S., I.M. Anderson, and D.L. Kohlstedt (2005) Influence of protons on Fe-Mg interdiffusion in olivine. *J. Geophys. Res.*, 110, doi: 10.1029/2004JB003292.

Hirose, K., N. Shimizu, W. Van Westrenen, and Y. Fei (2004) Trace element partitioning in Earth's lower mantle and implications for geochemical consequences of partial melting at the core-mantle boundary. *Phys. Earth Planet. Inter.*, 146, 249–260.

Hirth, G., and D.L. Kohlstedt (1996) Water in the oceanic upper mantle—implications for rheology, melt extraction and the evolution of the lithosphere. *Earth Planet. Sci. Lett.*, 144, 93–108.

Huang, X., Y. Xu, and S. Karato (2005) Water content of the mantle transition zone from the electrical conductivity of wadsleyite and ringwoodite. *Nature*, 434, 746–749.

Ingrin, J., and H. Skogby (2000) Hydrogen in nominally anhydrous upper-mantle minerals: Concentration levels and implications. *Eur. J. Mineral.*, 12, 543–570.

Inoue, T. (1994) Effect of water on melting phase relations and melt composition in the system Mg_2SiO_4-$MgSiO_3$-H_2O up to 15 GPa. *Phys. Earth Planet. Inter.*, 85, 237–263.

Inoue, T., and H. Sawamoto (1992) High pressure melting of pyrolite under hydrous condition and its geophysical implications. In Syono, Y., and M.H. Manghnani (eds.) High-Pressure Research: Application to Earth and Planetary Sciences, American Geophysical Union, Washington DC, pp. 323–331.

Inoue, T., D.J. Weidner, P.A. Northrup, and J.B. Parise (1998) Elastic properties of hydrous ringwoodite (γ-phase) of Mg_2SiO_4. *Earth Planet. Sci. Lett.*, 160, 107–113.

Jackson, I., J.D. Fitz Gerald, and H. Kokkonen (2000) High-temperature viscoelastic relaxation in iron and its implications for the shear modulus and attenuation of the Earth's inner core. *J. Geophys. Res.*, 105, 23605–23634.

Jackson, I., J.D. Fitz Gerald, U.H. Faul, and B.H. Tan (2002) Grain-size sensitive seismic-wave attenuation in polycrystalline olivine. *J. Geophys. Res.*, 107, doi: 10.1029/2002JB001225.

Jackson, I., M.S. Paterson, and J.D. Fitz Gerald (1992) Seismic wave dispersion and attenuation in Åheim dunite. *Geophys. J. Int.*, 108, 517–534.

Jacobsen, S.D., J.R. Smyth, H.A. Spetzler, C.M. Holl, and D.J. Frost (2004) Sound velocities and elastic constants of iron-bearing hydrous ringwoodite. *Phys. Earth Planet. Inter.*, 143/144, 47–56.

Jung, H., and S. Karato (2001a) Effect of water on the size of dynamically recrystallized grains in olivine. *J. Struct. Geol.*, 23, 1337–1344.

Jung, H., and S. Karato (2001b) Water-induced fabric transitions in olivine. *Science*, 293, 1460–1463.

Jung, H., I. Katayama, Z. Jiang, T. Hiraga, and S. Karato (2006) Effects of water and stress on the lattice preferred orientation in olivine. *Tectonophysics*, 421, 1–22.

Karato, S. (1974) Point defects and transport properties of olivine. MSc, University of Tokyo.

Karato, S. (1986) Does partial melting reduce the creep strength of the upper mantle? *Nature*, 319, 309–310.

Karato, S. (1989) Defects and plastic deformation in olivine. In Karato S., and M. Toriumi (eds.) Rheology of Solids and of the Earth, Oxford University Press, pp. 176–208.

Karato, S. (1990) The role of hydrogen in the electrical conductivity of the upper mantle. *Nature*, 347, 272–273.

Karato, S. (1995) Effects of water on seismic wave velocities in the upper mantle. *Proc. Jpn. Acad.* 71, 61–66.

Karato, S. (2000) Rheology and Dynamics of the Solid Earth, University of Tokyo Press.

Karato, S. (2003) Mapping water content in Earth's upper mantle. In Eiler, J.E. (ed.) Inside the Subduction Factory, American Geophysical Union, pp. 135–152.

Karato, S., D. Bercovici, G. Leahy, G. Richard, and Z. Jing (2006) Transition zone water filter model for global material circulation: Where do we stand? In Jacobsen S.D., and S. van der Lee (eds.) Earth's Deep Water Cycle, American Geophysical Union, submitted.

Karato, S., and H. Jung (2003) Effects of pressure on high-temperature dislocation creep in olivine polycrystals. *Philosophical Magazine, A.*, 83, 401–414.

Karato, S., M.S. Paterson, and J.D. Fitz Gerald (1986) Rheology of synthetic olivine aggregates: Influence of grain-size and water. *J. Geophys. Res.*, 91, 8151–8176.

Karato, S., and H.A. Spetzler (1990) Defect microdynamics in minerals and solid state mechanisms of seismic wave attenuation and velocity dispersion in the mantle. *Rev. Geophys.*, 28, 399–421.

Karato, S., S. Zhang, and H.-R. Wenk (1995) Superplasticity in Earth's lower mantle: Evidence from seismic anisotropy and rock physics. *Science*, 270, 458–461.

Katayama, I., H. Jung, and S. Karato (2004) New type of olivine fabric at modest water content and low stress. *Geology*, 32, 1045–1048.

Katayama, I., and S. Karato (2006a) Effect of water on low-temperature high-stress rheology of olivine. *J. Geophys. Res.*, submitted.

Katayama, I., and S. Karato (2006b) Effects of temperature on the B- to C-type fabric transition in olivine. *Phys. Earth Planet. Inter.*, in press.

Kohlstedt, D.L., H. Keppler, and D.C. Rubie (1996) Solubility of water in the α, β and γ phases of $(Mg,Fe)_2SiO_4$. *Contributions to Mineralogy and Petrology*, 123, 345–357.

Korenaga, J. (2003) Energetics of mantle convection and the fate of fossil heat. *Geophys. Res. Lett.*, 30, doi: 10.29/2003GL016982.

Korenaga, J. (2005) Firm mantle plumes and the nature of the core-mantle region. *Earth Planet. Sci. Lett.*, 232, 29–37.

Kubo, T., E. Ohtani, T. Kato, T. Shinmei, and K. Fujino (1998) Effects of water on the α–β transformation kinetics in San Carlos olivine. *Science*, 281, 85–87.

Kushiro, I., Y. Syono, and S. Akimoto (1968) Melting of a peridotite nodule at high pressures and high water pressures. *J. Geophys. Res.*, 73, 6023–6029.

Li, L., D.J. Weidner, P. Ratteron, J. Chen, and M.T. Vaughan (2004) Stress measurements of deforming olivine at high pressure. *Phys. Earth Planet. Inter.*, 143/144, 357–367.

Matsukage, K.N., Z. Jing, and S. Karato (2005) Density of hydrous silicate melt at the conditions of the Earth's deep upper mantle. *Nature*, 438, 488–491.

McCammon, C. (1997) Perovskite as a possible sink for ferric iron in the lower mantle. *Nature*, 387, 694–696.

Mei, S., and D.L. Kohlstedt (2000a) Influence of water on plastic deformation of olivine aggregates, 1. Diffusion creep regime. *J. Geophys. Res.*, 105, 21457–21469.

Mei, S., and D.L. Kohlstedt (2000b) Influence of water on plastic deformation of olivine aggregates, 2. Dislocation creep regime. *J. Geophys. Res.*, 105, 21471–21481.

Mibe, K., T. Fujii, and A. Yasuda (2002) Composition of aqueous fluid coexisting with mantle minerals at high pressure and its bearing on the differentiation of the Earth's mantle. *Geochim. Cosmochim. Acta*, 66, 2273–2285.

Montelli, R., G. Nolet, F.A. Dahlen, G. Masters, E.R. Engdhal, and S.H. Hung (2004) Finite-frequency tomography reveals a variety of plumes in the mantle. *Science*, 303, 338–343.

Nichols, A.R.L., M.R. Carroll, and A. Höskuldsson (2002) Is the Iceland hot spot also wet? Evidence from water contents of undegassed submarine and subglacial pillow basalts. *Earth Planet. Sci. Lett.*, 202, 77–87.

Nishihara, Y., T. Shinmei, and S. Karato (2006) Grain-growth kinetics in wadsleyite: Effects of chemical environment. *Phys. Earth Planet. Inter.*, 154, 30–43.

Nishihara, Y., D. Tinker, Y. Xu, Z. Jing, K.N. Matsukage, and S. Karato (2005) Plastic deformation of wadsleyite and olivine at high-pressures and high-temperatures using a rotational Drickamer apparatus (RDA). *J. Geophys. Res.*, submitted.

Nolet, G., S. Karato, and R. Montelli (2005) Plume fluxes from seismic tomography: A Bayesian approach. *Earth Planet. Sci. Lett.*, 248, 685–699.

Ochs, F.A.I., and R.A. Lange (1997) The partial molar volume, thermal expansivity, and compressibility of H_2O in $NaAlSi_3O_8$ liquid. *Contributions to Mineralogy and Petrology*, 129, 155–165.

Paterson, M.S. (1982) The determination of hydroxyl by infrared absorption in quartz, silicate glass and similar materials. *Bull. Mineral.*, 105, 20–29.

Paterson, M.S. (1989) The interaction of water with quartz and its influence in dislocation flow—an overview. In Karato S., and M. Toriumi (eds.) Rheology of Solids and of the Earth, Oxford University Press, pp. 107–142.

Paterson, M.S. (1990) Rock deformation experimentation. In Duba, A.G., W.B. Durham, J.W. Handin, and H.F. Wang (eds.) The Brittle-Ductile Transition in Rocks; The Heard Volume, American Geophysical Union, pp. 187–194.

Richard, G., M. Monnereau, and J. Ingrin (2002) Is the transition zone an empty water reservoir? Inference from numerical model of mantle dynamics. Earth Planet. Sci. Lett., 205, 37–51.

Shito, A., S. Karato, K.N. Matsukage, and Y. Nishihara (2006) Toward mapping water content, temperature and major element chemistry in Earth's upper mantle from seismic tomography. In Jacobsen S.D., and S.v.d. Lee (eds.) Earth's Deep Water Cycle, American Geophysical Union.

Shito, A., S. Karato, and J. Park (2004) Frequency dependence of Q in Earth's upper mantle inferred from continuous spectra of body wave. *Geophys. Res. Lett.*, 31, doi: 10.1029/2004GL019582.

Silver, L.A., and E.M. Stolper (1985) A thermodynamic model for hydrous silicate melts. *J. Geol.*, 93, 161–178.

Smith, M.F., and F.A. Dahlen (1981) The period and Q of the Chandler wobble. *Geophys. J. Roy. Astron. Soc.*, 64, 223–281.

Smyth, J.R. (1987) β-Mg_2SiO_4: A potential host for water in the mantle? *American Mineralogist*, 75, 1051–1055.

Smyth, J.R. (1994) A crystallographic model for hydrous wadsleyite (β-Mg_2SiO_4): An ocean in the Earth's interior. *American Mineralogist*, 79, 1021–1024.

Smyth, J.R., and D.J. Frost (2002) The effect of water on the 410-km discontinuity: An experimental study. *J. Geophys. Res. Lett.*, 29, doi: 10.129/2001GL014418.

Solomatov, V.S. (1996) Can hot mantle be stronger than cold mantle? *Geophys. Res. Lett.*, 23, 937–940.

Stixrude, L. (1997) Structure and sharpness of phase transitions and mantle discontinuities. *J. Geophys. Res.*, 102, 14835–14852.

van der Meijde, M., F. Marone, D. Giardini, and S. van der Lee (2003) Seismic evidence for water deep in Earth's upper mantle. *Science*, 300, 1556–1558.

Wallace, P. (1998) Water and partial melting in mantle plumes: Inferences from the dissolved H_2O concentrations of Hawaii basaltic magmas. *Geophys. Res. Lett.*, 25, 3639–3642.

Wang, W., and E. Takahashi (2000) Subsolidus and melting experiments of K-doped peridotite KLB-1 to 27 GPa; Its geophysical and geochemical implications. *J. Geophys. Res.*, 105, 2855–2868.

Wang, Y., W.B. Durham, I.C. Getting, and D.J. Weidner (2003) The deformation-DIA: A new apparatus for high temperature triaxial deformation to pressures up to 15 GPa. *Rev. Sci. Instrum.*, 74, 3002–3011.

Williams, Q., and R.J. Hemley (2001) Hydrogen in the deep Earth. *Ann. Rev. Earth Planet. Sci.*, 29, 365–418.

Wood, B.J. (1995) The effect of H_2O on the 410-kilometer seismic discontinuity. *Science*, 268, 74–76.

Xu, Y., Y. Nishihara, and S. Karato (2005) Development of a rotational Drickamer apparatus for large-strain deformation experiments under deep Earth conditions. In Chen J., Y. Wang, T.S. Duffy, G. Shen, and L.F. Dobrzhinetskaya (eds.) Frontiers in High-Pressure Research: Applications to Geophysics, Elsevier, Amsterdam, pp. 167–182.

Yamazaki, D., and T. Irifune (2003) Fe-Mg interdiffusion in magnesiowüstite up to 35 GPa. *Earth Planet. Sci. Lett.*, 216, 301–311.

Yamazaki, D., and S. Karato (2001a) High pressure rotational deformation apparatus to 15 GPa. *Rev. Sci. Instrum.*, 72, 4207–4211.

Yamazaki, D., and S. Karato (2001b) Some mineral physics constraints on the rheology and geothermal structure of Earth's lower mantle. *American Mineralogist*, 86, 385–391.

Yamazaki, D., T. Kato, E. Ohtani, and M. Toriumi (1996) Grain growth rates of $MgSiO_3$ perovskite and periclase under lower mantle conditions. *Science*, 274, 2052–2054.

Yamazaki, D., T. Kato, M. Toriumi, and E. Ohtani (2001) Silicon self-diffusion in $MgSiO_3$ perovskite at 25 GPa. *Phys. Earth Planet. Inter.*, 119, 299–309.

Yan, H. (1992) Dislocation Recovery in Olivine. Master of Science, University of Minnesota.

Young, T.E., H.W. Green, II., A.M. Hofmeister, and D. Walker (1993) Infrared spectroscopic investigation of hydroxyl in β-$(Mg,Fe)_2SiO_4$ and coexisting olivine: Implications for mantle evolution and dynamics. *Physics and Chemistry of Minerals*, 19, 409–422.

Yusa, H., and T. Inoue (1997) Compressibility of hydrous wadsleyite (β-phase) in Mg_2SiO_4 by high-pressure X ray diffraction. *Geophys. Res. Lett.*, 24, 1831–1834.

Zhao, Y.-H., S.B. Ginsberg, and D.L. Kohlstedt (2004) Solubility of hydrogen in olivine: Dependence on temperature and iron content. *Contributions to Mineralogy and Petrology*, 147, 155–161.