Mapping Water Content in the Upper Mantle: Mineral Physics Basis

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Water is known to affect a number of geochemical and geophysical processes but the water content in Earth’s interior is likely to vary both laterally and radially. This is particularly the case in subduction zones. Therefore if one can map water content from geophysical observations, it will contribute significantly to the better understanding of various geological processes. The fundamental prerequisite in doing is the understanding of how water affects geophysically observable quantities. In this presentation, I will review the current status of our understanding of effects of water on various physical properties of mantle minerals such as olivine. In addition to providing a brief summary of important well established points, I will try to identify critical issues on which further studies are urgently needed.

Perhaps the most important concept that mineral physics studies during the last ~20 years have established is that most of nominally anhydrous minerals can dissolve a significant amount of water (as hydrogen-related point defects) and that this dissolved water (i.e., hydrogen-related defects) has dramatic effects on a number of physical
properties. Compared to the effects of this dissolved water, effects through the presence of hydrous minerals are small when their amount is limited. Therefore I will focus on the effects of dissolved water in nominally anhydrous minerals such as olivine, rather than the effects through the presence of some hydrous minerals.

I will first review the current status of our understanding of how water (hydrogen) may be dissolved in nominally anhydrous minerals and then go on to review experimental and theoretical understanding of the effects of water on various physical properties. Finally, I will discuss how one can map water content in the mantle through geophysical observations.

I. Hydrogen-related defects in nominally anhydrous minerals

Experimental studies under well-constrained thermo-chemical conditions have established that a significant amount of water can be dissolved in nominally anhydrous minerals [for review see Bell and Rossman, 1992; Ingrin and Skogby, 2000]. The maximum amount of water that can be dissolved in these minerals is \( \approx 10^4 \) ppm H/Si (~0.1 wt%). Although this is significantly smaller than the amount of water that can be incorporated in some hydrous minerals (e.g., 3.3 wt% in hydrous wadsleyite, 4.7 wt% in talc, 4.3 wt% in phlogopite, 10.1 wt% in phase D), the amount of water that can be dissolved in nominally anhydrous minerals in the upper mantle is large and close to the amount of sea water.

Detailed experimental studies by several groups have established that “water” can be incorporated in nominally anhydrous minerals as hydrogen-related defects. A few points must be emphasized in relation to solubility of water and its effects on physical
properties. (1) The concentration of hydrogen-related (point) defects is significantly higher (by a factor of \(10^{-3}\)) than those of most abundant point defects in water-free minerals such as “dry” olivine. (2) The solubility (i.e., the concentration of hydrogen-related defects) increases with the fugacity of water [e.g., Bai and Kohlstedt, 1992; Kohlstedt et al., 1996]. (3) The water fugacity increases significantly with pressure because water is a highly non-ideal fluid [Pitzer and Sterner, 1994]. (4) Consequently, the effects of water on physical properties increase with pressure (water fugacity).

The experimental data on water fugacity – water solubility relationship provide bases to infer possible variation in water content in Earth. Important issues in this context include the partitioning of water among co-existing phases and their phase diagrams. One of these examples is the possible re-distribution of water associated with partial melting suggesting decrease in water content in olivine upon partial melting under water-undersaturated conditions [Karato, 1986; Hirth and Kohlstedt, 1996; Karato and Jung, 1998]. Another example is a high partition coefficient of water between wadsleyite and olivine [Smyth, 1987; Kohlstedt et al., 1996], implying a release of water associated with mantle upwelling across the 410km discontinuity. For the importance of the transition zone as a water reservoir, see also Kawamoto et al. [1996] and Bolfan-Casanova et al. [2000].

♦ Remaining issues

1. One of the remaining issues is the nature of water or hydrogen-related defects at grain-boundaries. There is evidence that a significant amount of water can be dissolved at or near grain boundaries and that water significantly enhances grain-boundary migration
[Jung and Karato, 2000a]. Characterizing amount of water at grain-boundaries and its role in modifying properties of grain-boundaries is an important issue.

2. Another issue is the partitioning of water between olivine and wadsleyite (probably ringwoodite as well). Recent studies show that most of the samples studied in laboratories are hydrous wadsleyite formed under water-saturated conditions in which 1/8 of the O1 site is occupied by OH and hence it is a distinct phase that can be written as $\text{Mg}_{1.75}\text{SiH}_{0.5}\text{O}_4$ [Kudoh et al., 1996]. In this case, water partitioning between wadsleyite and olivine so far determined (under water-undersaturated conditions) can be largely different from that determined under water saturated conditions. This issue has an important implication for the redistribution of water associated with the mass transport across the 410km discontinuity.

II. Effects of hydrogen-related defects on physical properties of minerals

(1) Electrical conductivity

Analysis of effects of water on electrical conductivity is rather straightforward once the nature of hydrogen-related defects is understood. Two mechanisms by which electrical conductivity can be enhanced may be distinguished. The first is the direct mechanism caused by the high concentration and high mobility of hydrogen (proton) in nominally anhydrous minerals such as olivine [Mackwell and Kohlstedt, 1990]. Such an effect can be evaluated from the well-established Nernst-Einstein relationship, viz.,

$$\sigma_c = f D cq^2 / kT$$

(1)
where $\sigma_c$ is electrical conductivity, $D$ is diffusion coefficient of charged species with charge $q$, $c$ is its concentration, $k$ is the Boltzmann constant and $T$ is temperature. Karato [1990] used this argument to show that the incorporation of hydrogen in olivine can significantly increase the electrical conductivity (Figure 1). Note that this effect is independent of changes in concentrations of other defects such as Fe$^{3+}$.

Another effect is an indirect effect through the increase in concentrations and/or the enhancement of mobility of other charged point defects. Karato et al. [1986] suggested that the diffusion coefficient of Mg (Fe) in olivine increases as a result of incorporation of hydrogen-related defects (see also Karato, 1989a). Both of these mechanisms could contribute to enhance electrical conductivity. The direct effect through proton charge transfer has lower activation enthalpy than that of Mg (Fe) diffusion and would dominate at relatively low temperatures. Also, the anisotropy in electrical conductivity is different between the two mechanisms.

♦ Remaining issues

Theoretical estimate of electrical conductivity from the Nernst-Einstein is straightforward and can be made without any assumptions. Therefore the notion that electrical conductivity in olivine is significantly enhanced by water is robust. However, no convincing experimental demonstration of effects of water has been performed yet. Part of the difficulties in experimental demonstration of the effects of water on electrical conductivity is to keep water (hydrogen) in the sample during an experiment. In these experiments, measurements of anisotropy in electrical conductivity will also be important, because it provides a strong constraint on the microscopic processes of electrical conductivity.
(2) Plastic deformation and deformation fabric (lattice preferred orientation)

The effects of water to enhance plastic flow in silicate minerals have long been known [for olivine Blacic, 1972; Chopra and Paterson, 1984; Mackwell et al., 1985; Karato et al., 1986; Mei and Kohlstedt, 2000a,b; Jung and Karato, 2000b]. Three important observations on olivine are of interest and will be discussed. First, when water is present, the effects of pressure on deformation are expected to be non-monotonous: pressure first enhances deformation due to the increase in water fugacity with pressure, but eventually pressure should suppress deformation due to the decrease in defect mobility under high pressures [Karato, 1989a]. Evidence of such a behaviour has recently been obtained in our laboratory [Jung and Karato, 2000b].

Second, increase in water fugacity also enhances grain-boundary mobility [Karato, 1989b; Jung and Karato, 2000a]. Jung and Karato [2000a] found that the size of dynamically recrystallized grains in olivine is significantly larger under high water fugacity conditions (Figure 2). In addition, their observations of dislocation microstructures suggest that water enhances grain-boundary mobility more than intragranular dislocation recovery processes.

Third, the effects of water to enhance deformation of olivine is highly anisotropic [Mackwell et al., 1985; Yan, 1992]: mobility of dislocations with Burgers vector $\mathbf{b}=[001]$ is much more enhanced by water than that of $\mathbf{b}=[100]$. This implies that deformation fabric (lattice preferred orientation) should change under high water fugacity conditions which could modify the relationship between deformation geometry and seismic anisotropy [Karato, 1995]. This hypothesis has been tested in our laboratory and we have obtained strong experimental evidence showing that the deformation fabric of olivine
under high water fugacity conditions is markedly different from well-known fabric under water-poor conditions (Figure 3) [Jung et al., 2000]. Under “dry” (water-free) conditions, olivine [100] direction becomes nearly parallel to shear direction and [010] direction nearly perpendicular to the shear plane [Zhang and Karato, 1995]. In contrast, under “wet” (high water fugacity) conditions, olivine [001] direction becomes nearly parallel to the shear direction and [100] direction nearly perpendicular to the shear plane. This change in fabric results in changes in seismic anisotropy. For example, $V_{SH}/V_{SV} > 1$ for horizontal shear under “dry” conditions, but $V_{SH}/V_{SV} < 1$ or ~1 under “wet” conditions. The change from “dry” fabric to “wet” fabric occurs at $X$(concentration of OH species)~1000 ppm H/Si. The change in fabric in olivine is likely to be due to the change in strain partitioning among different slip systems (slip along the [001] direction appears to become more important than slip along the [100] direction under “wet” conditions). However, deformation fabric under “wet” conditions has more complicated components. Based on the experimental observation that grain-boundary migration is enhanced by water more than the rate of recovery [Jung and Karato, 2000a], we consider that grain-boundary migration makes significant contribution to fabric development under “wet” conditions.

Well-known fabric of olivine is observed in rocks deformed in relatively shallow upper mantle (particularly oceanic upper mantle) where water content is believed to be small [Hirth and Kohlstedt, 1996; Karato and Jung, 1998]. According to the estimate by these authors, water content in typical asthenosphere is ~1000 ppm H/Si and water content in the asthenosphere of subduction zone could be ~3000 ppm H/Si. Therefore
deformation fabric and resultant seismic anisotropy under these conditions are likely to be different from those under sallow upper mantle condition.

♦ Remaining issues

Effects of water on deformation fabric in olivine have been investigated only very recently. We use shear deformation design as opposed to more conventional uni-axial (tri-axial) compression tests to obtain detailed data on fabrics. Although the deformation geometry is well-defined, stress orientation in samples in these experiments is not well constrained. Further improvement in experimental design and/or theoretical modeling of stress states in the experimental setting will be needed. Also, recent high-resolution measurements of fabric using EBSP show that the deformation fabric in olivine is in general more complicated than previously thought [Lee and Karato, 2000]. More detailed studies are needed to fully characterize deformation fabric and to justify extrapolations to geological conditions.

(3) Attenuation and velocities of seismic waves

Water dissolved in minerals can affect the velocity and attenuation of seismic wave propagation. The most direct effect of water is the reduction of bond strength which results in slower seismic wave velocities. Although such an effect is significant (several %) in hydrous wadsleyite and ringwoodite [Yusa and Inoue, 1997; Inoue et al., 1999], such effects are much smaller for olivine where the maximum amount of dissolved water is significantly smaller [Kohlstedt et al., 1996]. Therefore this direct effect can be neglected in the upper mantle. However, indirect effects caused by enhanced anelasticity can be significant. Although not comprehensive yet, existing experimental data [Jackson
et al., 1992] and microscopic models of anelasticity strongly indicate that water enhances anelasticity [Karato, 1995].

The effects of water to modify seismic wave propagation can be formulated using the following relationships. First, water can affect seismic wave attenuation (Q-factor) through,

\[ Q^{-1}(\omega, T, P, C_{\text{OH}}) = D(A + BC_{\text{OH}})^{\alpha} \exp[-\alpha(E^* + PV^*)/RT] \] (2)

where \( Q^{-1} \) is attenuation factor, \( \omega \) is frequency of seismic waves, \( \alpha (0.1-0.3) \) is a parameter that characterizes the frequency dependence of \( Q \), \( D, A, B \) are constants, \( C_{\text{OH}} \) is the concentration of \( \text{OH} \) species in mineral (olivine), \( E^* \) and \( V^* \) are the activation energy and volume for attenuation, \( P \) is pressure, and \( R \) is the gas constant.

A change in \( Q \) results in a change in seismic wave velocities, viz.,

\[ V(\omega, T, P, C_{\text{OH}}) = V_o(T, P)[1 - FQ^{-1}(\omega, T, P, C_{\text{OH}})] \] (3)

where \( V \) is the velocity of seismic waves, \( V_o \) is the velocity of seismic waves at infinite frequency where effects of anelasticity are negligible and \( F \) is a constant with order unity. The terms in the square bracket indicates the correction for the effects of anelasticity. The point is that effects of anelasticity on seismic wave propagation is large in regions of high attenuation (low \( Q \)), and that the degree to which anelasticity affects seismic wave propagation changes with water content. Therefore, the effects of variation in water content (water fugacity) on seismic wave propagation are expected to be significant in the
wedge mantle above subducted oceanic lithosphere. The spatial variation in seismic wave velocities and attenuation in these regions should partly be due to the variation in water content as well as temperature.

Increased water fugacity can sometimes lead to partial melting. Obviously partial melting can significantly affect seismic wave propagation directly through reduced strength of molten portions as well as indirectly through the re-distribution of water [Karato and Jung, 1998].

♦ Remaining issues

Direct laboratory studies of effects of water on anelasticity are admittedly sketchy although recent experimental studies on attenuation and deformation (and related processes) strongly suggest that water significantly enhances anelasticity. More detailed experimental studies are critically needed in this area.

III. Mapping water content in the upper mantle: Outlook

Given the relationships between water content and physical properties in minerals, we would be able to map the water content in Earth’s interior from geophysical observations. The current knowledge on the role of water on physical properties strongly suggests that water in nominally anhydrous minerals (such as olivine) has important effects on a number of physical properties. In many cases, the effects of high water content are similar to those of high temperatures (e.g., high electrical conductivity, high attenuation and low seismic wave velocities). In some other cases, the effects of water are qualitatively different from those of temperatures. Effect of water on deformation fabrics of olivine is a good example.
Thus, I emphasize the following two points. (1) Based on mineral physics studies in various laboratories, it is now clear that the effects of water (through hydrogen-related defects) on physical properties are large and can be detected by some geophysical measurements. (2) However, various other factors such as temperature could also modify physical properties, and an important issue is how to distinguish the effects of water from effects of other variables.

I will discuss some issues of how to separate the effects of water from those of other variables using anomalies in seismic velocities (and attenuation) as examples. Issues to be discussed include how to separate temperature effects from water effects and how to separate effects of flow geometry from the effect of water content.
References


Figure 1. Effects of water on electrical conductivity in olivine [Karato, 1990].
Figure 2. Dynamically recrystallized grain-size versus stress relationship in olivine [Jung and Karato, 2000a]. The size of dynamically recrystallized grains is significantly larger under water-rich (“wet”) conditions than that under water-poor (“dry”) conditions.
Figure 3. Lattice preferred orientation in olivine deformed by simple shear under water-rich ("wet") and water-poor ("dry") conditions [Zhang and Karato, 1995; Jung et al., 2000]. Both samples were deformed to ~120% shear strain. The dry sample was deformed at $T=1573$ K ($P=300$ MPa), strain-rate $\sim 10^{-4}$/s, and the wet sample was deformed at $T=1473$ K ($P=2$ GPa), strain-rate $\sim 10^{-3}$/s.