

Nominally Anhydrous Minerals and Earth's Deep Water Cycle

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Deep reservoirs of water incorporated as hydroxyl into solid silicate minerals of the Earth's interior may contain the majority of the planet's hydrogen and have acted as buffers to maintain ocean volume and continental freeboard over geologic time. Two tenths of one weight percent H₂O in subducted oceanic crustal material and subsequently released to the hydrosphere from mid-ocean ridge basalt is sufficient to recycle the total ocean volume once over 4.5 billion years. It is possible that actual fluxes are several times this amount. The nominally anhydrous minerals of the transition zone (410–660 km depth) may serve as a large internal reservoir. New and recent data on molar volumes and elastic properties indicate that hydration has a larger effect on shear velocities than does temperature within their respective uncertainties. Based on these new data, seismic velocities in this region are consistent with significant hydration (one-half percent or more H₂O by weight in a pyrolite-composition mantle). The data indicate that lateral velocity variations in the Transition Zone (TZ) may reflect variations in hydration rather than variations in temperature, at least in regions distant from subduction zones.

1. INTRODUCTION

Earth is unique among the Terrestrial planets in having liquid water on its surface. Water controls the entire character of the biology and geology of the planet. Without liquid water, carbon-based life is highly unlikely if not impossible. Geologically, water controls igneous activity by lowering the melting points of rocks by hundreds of degrees Celsius. It fluxes melting below divergent plate boundaries [*Asimow and Langmuir*, 2003] and controls major-element partitioning [*Inoue*, 1994]. Water controls tectonics by affecting the strength and deformation mechanisms of minerals [*Kavner*,

2003] and thus the rheology of rocks [*Karato*, 1998; *Mei and Kohlstedt*, 2000]. It also controls weathering and all low temperature geochemical reactions that generate sediments from rocks. Water transports the sediments in streams and glaciers, and deposits them in rivers, lakes, and oceans. Although oceans cover more than seventy percent of the surface, they constitute only 0.025 percent of the planet's mass. The presence of quartz pebble conglomerates of earliest Archean age tells us that there has been moving water on the surface, hence oceans and dry land, almost as far back as we can see in geologic time. Oxygen isotope ratios in ancient detrital zircons indicate the presence of liquid water as early as 4.4 GY ago [*Wilde et al.*, 2001; *Mojzsis et al.*, 2001]. Although Earth's oceans are unique in our solar system, how common might Earth-like water planets be in our galaxy or in other galaxies?

Despite its importance to understanding the biology and geology of the planet, hydrogen is the most poorly constrained major-element compositional variable in the bulk Earth. The total complement of Earth's hydrogen is unknown within an order of magnitude [Abe *et al.*, 2000]. We do not have good constraints on the amount of H that may be incorporated in hydrated ocean crust and lithospheric mantle [Dixon *et al.*, 2002] or in interior reservoirs, particularly in the transition zone [Richard *et al.*, 2002], but also in the deep mantle and core [Williams and Hemley, 2001]. Further, the origin of the hydrogen on the planet is a subject of considerable debate. Is it endogenous, part of the planet's original accretion of material [Drake and Richter, 2001], or exogenous, added after accretion and differentiation from relatively D-enriched comets [Robert, 2001; Delsemme, 1999]? Has ocean volume been relatively constant over geologic time as is widely assumed, or has it fluctuated significantly? Is there a large reservoir of hydrogen incorporated in solid silicate minerals in the interior [Smyth, 1987; Bercovici and Karato, 2003], or is the interior relatively dry [Dixon and Clague, 2001; Wood, 1995]? What are the fluxes of water into and out of the uppermost (<200 km) [Iwamori, 1998; Schmidt and Poli, 1998] and deeper mantle (>200km) [Schmidt, 1996; Kawamoto *et al.*, 1996]? Such questions can be and have been addressed through various Earth Science sub disciplines, but as yet there is relatively little sense of consensus.

Hirschmann *et al.* [2005] have estimated the H storage capacities of the nominally anhydrous minerals in the various regions of the upper mantle, transition zone, and lower mantle. Recent results on the hydration of olivine indicating H₂O contents approaching one percent by weight [Smyth *et al.*, 2006; Mosenfelder *et al.*, 2006] at temperatures and pressures near the 410 km discontinuity, suggest that there may be a significant flux of water into the transition zone and perhaps the lower mantle as hydroxyl in the nominally anhydrous silicates of the region. An assessment of the hydration of the upper mantle and transition zone will depend on measurements of the molar volume, bulk moduli and full elastic properties of these phases as a function of water content. Such data are far from complete, but preliminary findings indicate that hydration may have a larger effect on these properties than does temperature within the uncertainties of each. The objective of this paper is to review the effects of hydration on the physical properties of these phases and provide a preliminary assessment of the possibility of a deep water cycle within the mantle. To estimate the significance of a deep water cycle, we begin with a review of the possible fluxes and potential reservoirs in the nominally anhydrous minerals of the upper mantle and transition zone.

2. FLUXES AND RESERVOIRS

The current flux of crustal material into the deep mantle (> 200 km depth) with subduction must be approximately equal to the amount of new ocean crust generated from mantle sources at mid-ocean ridges plus small amounts of ocean island basalts. If the total length of mid-ocean ridge is 70,000 km, the average spreading rate 10 cm per year [Gordon, 1995], and the average ocean crust thickness is 7 km [Parsons, 1982], then approximately 49 km³ of crust is created and consumed per year. Alternatively, if the total area of oceanic crust on the Earth is 3.6 x 10⁸ km², and it has a mean age of 80 million years [Parsons, 1982], we estimate 32 km³ per year. If this material were 0.1 percent water by weight, it would be 0.3 percent water by volume for a net flux of about 0.1 to 0.15 km³ per year of liquid-water equivalent. If subduction rates have been constant over the past 4.5 billion years, the integrated volume is equal to about one-half the entire current ocean volume. In other words, 0.2 percent water by weight (2000 ppmw) in deeply subducted crust (i.e., just the crustal portion of the slab) and returning in mid-ocean ridge basalt is roughly sufficient to recycle the ocean once in 4.5 billion years, assuming current subduction and spreading rates. It is likely that subduction rates were higher in the past, so it is probable that geologically significant amounts of H have been carried to the interior over geologic time. Also, hydration is likely to extend well into the oceanic lithosphere, and Wen and Anderson [1995] estimate an annual flux of lithosphere of 265 km³. Furthermore, water released by dehydration of the subducting slab below 200 km depth, will likely be captured by the hot olivine in the overlying mantle wedge. Hydration greatly reduces the strength and effective viscosity of olivine [Karato *et al.*, 1986] allowing it to lubricate the downward movement of the cold slab. Mid-ocean ridge basalt (MORB) liquids contain anywhere from 0.1 to 1.5 weight percent H₂O, but are generally thought to average 0.25 percent by weight [Dixon *et al.*, 2002]. Eclogites from kimberlites and ultra-high pressure metamorphic zones that are thought to represent subducted crustal material, contain comparable amounts of water [Rossman and Smyth, 1990; Smyth *et al.*, 1991; Katayama and Nakashima, 2003]. Thus, if the total ocean volume has not been increasing over geologic time, it probably represents some equilibrium exchange volume with an internal reservoir contained as hydroxyl in silicate minerals of the mantle at depths greater than about 200 km.

Hydrated oceanic crust ranges up to nearly 8 percent and averages 1.0 to 1.5 percent by weight H₂O [Alt, 2004]. Major hydrous minerals in the hydrated crust include iron oxy-hydroxides, celadonite, and saponite at low tempera-

ture and talc, chlorite, lawsonite, and amphiboles at higher temperatures. Below the basalts and gabbroic sheeted dikes, lie cumulate gabbros and ultramafic rocks. Most of nominally hydrous minerals of the crustal portion of the slab break down before the slab reaches the 410 km discontinuity, and much of this water is returned via arc volcanism. Talc and chlorite dehydrate at relatively low pressures (< 3GPa), whereas lawsonite and phlogopite are stable to about 7 GPa on a cold geotherm [Kawamoto *et al.*, 1996, Schmidt and Poli, 1998]. Talc breaks down to 10Å-phase and eventually to phase E or will dehydrate to enstatite. Phengite however is stable to 11 GPa (330 km) [Schmidt, 1996] but requires the presence of potassium. As mentioned earlier, the nominally anhydrous minerals of eclogite can contain 1000 to 2000 ppmw H₂O.

Below the crust, the lithospheric mantle is composed of harzbergites and peridotites. Hydrothermal alteration of the ultramafic rocks produces mainly serpentine and talc. Serpentine and chlorite contain roughly ten percent water by weight or nearly 30 percent by volume, so a fully hydrated oceanic lithosphere could sequester more than one entire ocean volume of water. If hydration of the lithospheric mantle is significant, the amount of water being subducted may be larger. The major hydrous minerals of ultramafic rocks include serpentine, talc, chlorite, and amphibole. Talc and chlorite break down at shallow depths (< 100 km), but serpentine and amphibole are stable to 200 km or more in a cold subduction geotherm [Kawamoto *et al.*, 1996]. Serpentine breaks down to phase A and eventually to clinohumite plus olivine.

The breakdown of these minerals can release potentially very large amounts of aqueous fluids, which can cause flux melting in the overlying hot mantle wedge. Dixon *et al.* [2002] have argued that dehydration is highly efficient with 99 percent of water from igneous rocks and 97% from sediments being returned, on the basis of the incompatible behavior of hydrogen in these systems. This estimate ignores the H contents of nominally anhydrous minerals and the pressure effect on the compatibility of H, and so may be a high estimate of the dehydration efficiency. The amount of residual water remaining in the slab would be significant given the volumes of subducted material. About 2000 ppmw in the crustal portion of the slab alone (~90% efficiency) would be sufficient to recycle the current ocean volume once in 4.5 billion years at current subduction rates. The more rapid the subduction, the cooler the slab and the deeper the nominally hydrous phases are stable. The amount of H soluble in olivine increases at least a hundred-fold relative to ambient conditions at pressures above 10 GPa (300 km) [Kohlstedt *et al.*, 1996; Locke *et al.*, 2002, Mosenfelder *et al.*, 2006; Smyth *et al.*, 2006], meaning that

at high pressure, hydrogen is a more compatible element than is commonly believed. If there is significant hydration of the lithospheric mantle below the crust, the flux would be larger, as it would be if there were significant capture of H by olivine in the hot mantle wedge overlying the slab. If subduction rates in the early Earth were much higher than at present, H fluxes would have been higher in the past.

In the Transition Zone, water can be held in the wadsleyite and ringwoodite phases. Wadsleyite is known to incorporate up to 3.0 wt% , and ringwoodite 2.8 wt% H₂O [Kohlstedt *et al.*, 1996]. A mantle of 75 percent olivine-stoichiometry (i.e., pyrolite) would then be able to incorporate some eight times the ocean volume in the Transition Zone before the nominally anhydrous phases become saturated. The amount of H₂O in both wadsleyite and ringwoodite decreases with temperature above 1100°C, but there is still a nearly percent H₂O at 1400°C [Demouchy *et al.*, 2005; Smyth *et al.*, 2003]. The experimental evidence is now indisputable that these silicates are capable of incorporating globally significant amounts of water, but the actual H-content (or hydration state) of the Transition Zone is unknown. In order to evaluate how much water might actually be present, careful laboratory measurements of the effects of hydration on transformation pressures, and molar volume and elastic properties of these minerals will be required. These data can then be compared with seismic models of the interior. Such measurements are in progress, but are by no means complete.

3. VOLUMES OF HYDRATION

Hydration has a significant effect on the molar volume of the nominally anhydrous phases of the upper mantle and transition zone. Smyth *et al.* [2006] report that 0.5 percent by weight H₂O in olivine has about the same effect on density as raising the temperature by 240°C. Smyth *et al.* [2006] give unit cell volume data for forsterite as a function of H₂O contents, based on the olivine-specific calibration of Bell *et al.* [2003]. Converting their data to molar volumes for comparison with wadsleyite and ringwoodite and fitting their data to a linear relation we obtain

$$MV = 14.67241 (\pm 0.00078) + 2.07 (\pm 0.15) \times 10^{-6} * c_{\text{H}_2\text{O}} \quad [1]$$

with a correlation coefficient, R, of 0.86, where MV is molar volume in cm³ and c_{H₂O} is the ppm by weight H₂O as determined from FTIR using the calibration of Bell *et al.* [2003] for polarized infrared spectra. This calibration give H₂O contents nearly three times those of the general (unpolarized) calibrations of Libowitzky and Rossman [1997] or Patterson [1982].

Jacobsen et al. (2005) and Holl et al. (2003) give cell volume data for wadsleyite as a function of H₂O content. Fitting these data to a linear relation, we obtain

$$MV = 13.61674 (\pm 0.00038) + 1.43 (\pm 0.05) \times 10^{-6} * c_{\text{H}_2\text{O}} \quad [2]$$

with a correlation coefficient, R, of 0.96. H₂O contents were determined based on the general infrared calibration Libowitzky and Rossman [1997] which is close to that of Patterson [1981].

Similarly, Smyth et al. [2003] give volume data for pure magnesian ringwoodite as a function of H₂O content. From these data we obtain:

$$MV = 13.2478 (\pm 0.0018) + 4.75 (\pm 0.35) \times 10^{-6} * c_{\text{H}_2\text{O}} \quad [3]$$

with a correlation coefficient, R, of 0.99. These data indicate similar relative volume expansion with hydration for olivine and wadsleyite and a larger expansion for ringwoodite. If the cell volume data of Kudoh et al. [1998] for a sample with estimated 20000 ppmw H₂O is included is included, the volume effect is larger, as are the errors in the regression. This relation is based on H₂O determination by infrared spectroscopy and therefore dependent on the calibration used. The relative

volume expansions as a function of H₂O content at ambient conditions for forsterite, wadsleyite, and ringwoodite are plotted in Figure 1. The H contents of wadsleyite and ringwoodite used for these volume effect estimates are based on the general calibrations and may be subject to revision if phase-specific calibrations are subsequently developed for wadsleyite and ringwoodite. These volumes should not be used to estimate the buoyancy of hydrous materials in the Earth, because we do not yet have experimental measurements of the effect of hydration on thermal expansion and compressibility, but work is proceeding rapidly in this area as outlined below.

4. ELASTIC PROPERTIES

Bulk modulus measurements on hydrous ringwoodite [Inoue et al. 1998; Smyth et al. 2004], hydrous wadsleyite [Crichton et al., 1999; Smyth et al., 2005b; Holl et al., 2003], and olivine [Smyth et al., 2005a; 2006] indicate significant softening with hydration. Unit cell volume measurements as a function of pressure yield an isothermal bulk modulus measurement, K_T, as well as a value for K' (dK/dP), if the volume measurements are of sufficient precision. In general, the effect of hydration on these phases is to decrease bulk

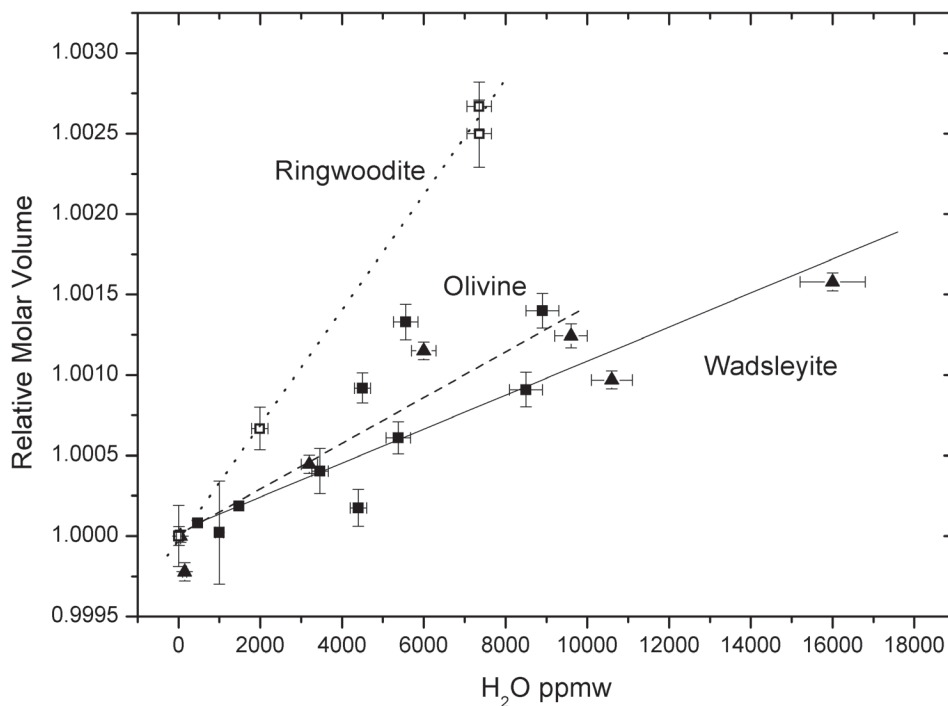


Figure 1. Relative molar volume expansions at ambient conditions with hydration for olivine, wadsleyite, and ringwoodite. The larger expansion effect observed for ringwoodite may be due to a larger role of tetrahedral vacancy in the hydration of ringwoodite relative to wadsleyite and olivine. The flexure in the expansion curve of wadsleyite correlates with the decrease in space group symmetry from *Imma* to *I2/m*.

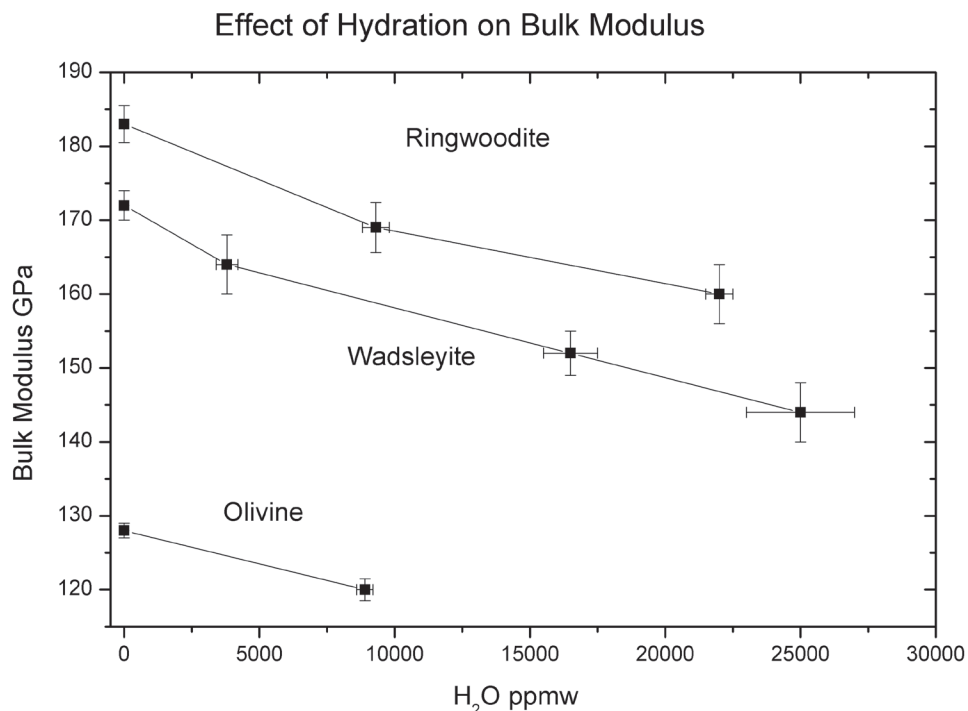


Figure 2. Effect of hydration on isothermal bulk modulus at ambient conditions for olivine, wadsleyite, and ringwoodite.

modulus and increase K' . We have plotted the isothermal bulk modulus values for olivine, wadsleyite, and ringwoodite as a function of H_2O content in Figure 2. For anhydrous samples we use values of 128 GPa for olivine [Will *et al.*, 1986; Kudoh and Takéuchi 1985, Downs *et al.*, 1996], 172 GPa for wadsleyite [Hazen *et al.*, 2000], and 183 GPa for ringwoodite [Zerr *et al.*, 1993]. A preliminary value of the bulk modulus for hydrous olivine is 120 GPa from Smyth *et al.* [2005a], and for hydrous wadsleyite we use 162 GPa (~ 1 wt% H_2O) and 155 GPa (~ 2.5 wt% H_2O) from Holl *et al.* [2003] and Yusa and Inoue [1997]. For ringwoodite, values are 175 GPa (~ 1 wt% H_2O) and 165 GPa (~ 2.8 wt% H_2O) from the studies of Manghnani *et al.* [2005] and Wang *et al.* [2003]. The data indicate similar elastic softening of all three phases. Bulk modulus measurements alone do not yield values for V_p and V_s , however full elastic property measurements for hydrous ringwoodite are available and may give some indication of the effects for olivine and wadsleyite.

Elastic property measurements on hydrous ringwoodite at ambient conditions [Wang *et al.*, 2003; Jacobsen *et al.*, 2004a], and at elevated pressure [see Jacobsen and Smyth, this volume] also indicate significant reduction of both bulk and shear moduli with hydration. The high-pressure acoustic measurements on hydrous ringwoodite were made using a novel GHz-ultrasonic method [Jacobsen *et al.*, 2004b], where measured velocities (V_p and V_s) in various crystal-

lographic orientations were used to determine the complete elastic tensor of the single crystals grown at high pressure. Aggregate moduli were fit to the single-crystal elastic data up to 10 GPa, resulting in $K_{S0} = 177(4)$ GPa, $K_S' = 5.3(4)$, $G_0 = 103(1)$ GPa and $G' = 2.0(2)$ for the ringwoodite of Fe_{90} composition and containing ~ 1 wt% H_2O [see Jacobsen and Smyth, this volume]. In agreement with static compression measurements [Manghnani *et al.*, 2005], the bulk modulus of ringwoodite is reduced by about 6% upon hydration. The shear modulus is reduced by about 12%, indicating that water has a greater affect of shear properties. At ambient conditions, the magnitude of reduction is large; adding 1 wt% H_2O into ringwoodite has the same effect on V_p and V_s as raising the temperature by about 600°C and 1000°C, respectively. Due to elevated pressure derivatives, the difference between anhydrous and hydrous velocities diminishes, but temperature derivatives of the moduli are still needed to make a more accurate evaluation of the effects of water on velocities in the transition zone.

To illustrate the magnitude of effects of ~ 1 wt% H_2O hydration on velocity we have calculated monomineralic P and S velocities for hydrous and anhydrous ringwoodite and wadsleyite using finite strain equations of state [Davies and Dziewonski 1975] along an adiabat with 1673 K foot temperature (Plate 1). For comparison, we also show several global velocity models; PEMC [Dziewonski *et al.*, 1975], PREM

[Dziewonski and Anderson 1981], and IASPEI91 [Kennett and Engdahl, 1991]. For anhydrous phases we use K_s values of 129, 172, and 188 GPa with dK_s/dP of 4.3 for all three phases [Duffy et al., 1995; Li et al., 1998; Sinogeikin et al., 2003; and Li, 2003]. We use shear moduli (G) of 82, 106, and 120 GPa for dry olivine, wadsleyite, and ringwoodite with dG/dP of 1.4 [Duffy et al., 1995; Li et al., 1998; Sinogeikin et al., 2003; Li, 2003]. The parameters for hydrous ringwoodite are from our measurements, and those of hydrous wadsleyite are scaled from our measurement on ringwoodite. We assume pressure derivatives for the hydrous phases are increased to 5.3 for K' and 1.8 for G' . For comparison, we also plot velocities for majorite garnet using $\rho_0 = 3.53 \text{ kg/m}^3$, $K_{S0} = 165 \text{ GPa}$ and $G_0 = 88 \text{ GPa}$ [Gwanmesia et al., 1998; Sinogeikin et al., 1997] with $dK_s/dT = -0.020$ and $dG/dT = -0.010$ [Suzuki and Anderson 1983] and assuming pressure derivatives of $K' = 4.3$ and $G' = 1.4$. Given the absence of temperature derivatives of the moduli for the hydrous phases, in this simple model we are required to assume anhydrous values. Temperature dependence of the bulk modulus (dK_s/dT) was taken to be -0.016 GPa/K for dry olivine [Liu et al., 2005], -0.019 GPa/K for dry wadsleyite [Li et al., 1998; Katsura et al., 2001], and -0.021 GPa/K for dry ringwoodite [Sinogeikin et al., 2003; Mayama et al., 2005]. Temperature dependence of the shear modulus (dG/dT) was taken to be -0.013 GPa/K for dry olivine [Liu et al., 2005], -0.017 GPa/K for dry wadsleyite [Li et al., 1998; Katsura et al., 2001], and -0.015 GPa/K for dry ringwoodite [Sinogeikin et al., 2003; Mayama et al., 2005]. A linear coefficient of volume thermal expansion $\alpha_v = 27 \times 10^{-6} \text{ K}^{-1}$ was assumed for all phases. The set of thermoelastic parameters used in this illustrative model are given in Table 1.

Whereas elevated pressure derivatives act to bring hydrous and anhydrous P-wave velocities to within their mutual uncertainty in the transition zone, S-wave velocities for the hydrous phases remain several percent lower than anhydrous S-wave velocities. Temperature derivatives of the elastic moduli for the hydrous phases will be needed in order to improve estimates of hydrous velocities in the transition zone. Considering the current model, S-wave velocities for both hydrous and anhydrous velocities for wadsleyite match

the seismic velocity models equally well, whereas in the deeper part of the TZ where ringwoodite is the stable phase, hydrous ringwoodite, or a mixture of anhydrous ringwoodite and majorite best fit the velocity models. The key feature of Plate 1 is that both reduced S-wave velocities, and elevated V_p/V_s ratios are generally indicative of hydration.

5. DISPLACEMENT OF TRANSITIONS

There are several possible ways to detect hydration (or lateral variations of water) in Earth's Transition Zone, and, as outlined above, there has been much recent progress in quantifying the physical properties of hydrous high-pressure phases to make this possible. The seismic discontinuities at 410, 525, and 660 km depths correspond to phase transitions in the Mg_2SiO_4 phases (olivine, wadsleyite, ringwoodite) composing 50 to 80 percent of the upper mantle and TZ [Duffy et al., 1995; Duffy and Anderson, 1989]. Water can affect not only the seismic velocities, but also the depths of transitions, and the width or sharpness of the transitions in these phases [Wood, 1995; Smyth and Frost, 2002; Chen et al., 2002; Hirschmann et al., 2005, also see Hirschmann et al., this volume]. These are the major seismic observables that can be evaluated in the laboratory. The absolute thickness of the TZ (between 410 and 660 km) can be determined more accurately than the absolute depth of the discontinuities using the relative arrival times of P-to-S converted phases [Gilbert et al., 2003]. Because water is more soluble in wadsleyite and ringwoodite than in either olivine above the TZ or perovskite plus ferropericlase below the TZ, we expect H to expand the wadsleyite and ringwoodite stability fields relative to olivine at 410 and perovskite plus ferropericlase at 660 km [Wood, 1995]. The olivine to wadsleyite transition is exothermic with a positive Clapeyron slope (dP/dT), so hydration and decreased temperature have similar effects; moving the olivine-wadsleyite transition (410 km) to shallower depths, whereas the negative Clapeyron slope of the ringwoodite-perovskite transition (660 km) would move it to deeper depths. Smyth and Frost [2002] indeed observed a decrease in the pressure of the olivine-wadsleyite transition of about 1.0 GPa ($\sim 30 \text{ km}$) with the addition of 2 wt%

Table 1. Thermoelastic Properties of Hydrous and Anhydrous (10,000 ppmw H_2O) Polymorphs of $(\text{Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4$

	ρ_{STP} (g/cm^3)	K_s (GPa)	dK_s/dP	dK_s/dT (GPa K^{-1})	G (GPa)	dG/dP	dG/dT (GPa K^{-1})
Olivine	3.36	129	4.3	-0.016	82	1.4	-0.013
Wadsleyite (dry)	3.57	172	4.3	-0.019	106	1.4	-0.017
Wadsleyite (wet)	3.51	155	5.3	-0.019	93	1.8	-0.017
Ringwoodite (dry)	3.70	188	4.3	-0.021	120	1.4	-0.015
Ringwoodite (wet)	3.65	177	5.3	-0.021	105	1.8	-0.015

H₂O into the system. However, hydration and decreased temperature have the opposite effect on the seismic velocities of the intervening transition zone; decreased temperature increases P and S-wave velocities, whereas hydration decreases these velocities. Therefore, a slow (red) and thick TZ would suggest the presence of water (Plate 2). In order to further distinguish the effects of temperature and hydration, it is important to evaluate the relative magnitudes of these effects on P and S velocities. Results of Jacobsen and Smyth [*this volume*] indicate that hydration has a larger effect on V_s than on V_p in ringwoodite. A systematic search for regions of anti-correlation of the depths to the 410 and 660 km discontinuities and estimation of intervening seismic velocities, and in particular elevated V_p/V_s ratios, might reveal region of significant hydration in the transition zone. Such a search is beyond the scope of the current study.

6. DISCUSSION

The pyrolite model of mantle composition and mineralogy was developed by Ringwood [1976] to be a single composition throughout the upper and lower mantle that is roughly consistent with a bulk Earth of chondritic composition, with phase transformations observed in the laboratory, with velocities and densities derived from seismology, with high pressure inclusions seen in basalts and kimberlites, and to yield basalt by partial melting. The model has more than 60% normative olivine. Are observed velocities in the TZ consistent with significant hydration (i.e. >0.1 wt % H₂O) of this composition? The velocity jump at 410 km observed seismically is too small to be consistent with an olivine to wadsleyite transition in a dry, olivine-rich (pyrolite) mantle [Duffy and Anderson, 1989; Anderson, 1989; Anderson and Bass, 1986]. The small velocity increase at 410 km led these authors to suggest that the mantle in this region must have less than 50% olivine. However, the current ultrasonic results together with static compression measurements indicate a dramatic decrease in elastic stiffness of wadsleyite and ringwoodite with hydration [Crichton *et al.*, 1999; Duffy *et al.*, 1995; Yusa and Inoue, 1997; Smyth *et al.*, 2004]. This means that the observed velocity jump at 410 km would be more consistent with a hydrous than an anhydrous mantle for an olivine-rich stoichiometry, i.e. pyrolite, with more than 60% normative olivine.

Several authors have pointed out that the observed velocities in the transition zone are inconsistent with a dry pyrolite composition mantle [Duffy *et al.*, 1995; Duffy and Anderson, 1989; Anderson, 1989; Anderson and Bass, 1986]. However, it can be seen from Plate 1 that the very large effect of hydration on the P and S velocities in ringwoodite and inferred for wadsleyite, means that PREM model velocities are consistent

with a pyrolite-composition Transition Zone with one-half to one weight percent H₂O. Because of its very high diffusive mobility and fractionation into melt phases, hydrogen could be effectively decoupled from other compositional variables, that is, exhibit open system behavior. Wood (1995) argued that the sharpness of the 410 km discontinuity precludes water contents above 0.025% by weight. However, gravity-driven diffusion of H would likely sharpen the olivine-wadsleyite boundary [Smyth and Frost, 2002] in regions without strong vertical convection, and the presence of a small amount of partial melt [Bercovici and Karato, 2003] or a mobile aqueous fluid, could sharpen even a convecting boundary. It is therefore unlikely that the observed width of the 410 km discontinuity will provide a strong constraint on the amount of H present. Although hydrogen diffusion rates for wadsleyite and ringwoodite remain unknown, they must be less than the diffusion rate for heat and so simple diffusion cannot compete with convection for redistribution of H on a global scale [Richard *et al.*, 2002].

In summary, the observation of the very strong effect of hydration on P and S velocities in ringwoodite, and inferred from isothermal compression of wadsleyite, indicate that hydration is likely to have a larger effect on seismic velocities than temperature within the uncertainties in each in the Transition Zone. This means that tomographic images of the transition zone in regions distant from active subduction, blue coloration (fast) is more likely to indicate dry than cool, and red (slow) is more likely to indicate wet, than hot. Seismic data are consistent with a transition zone hydration between 0.5 and 1.0 weight percent H₂O for a pyrolite-composition model. This estimate is based on some simple assumptions about the effect of temperature and pressure on the elastic properties of the major hydrous phases (Table 1) which are not yet well constrained by experimental data. Hydrogen abundance at the higher end of this estimate would be sufficient to generate the small amount of partial melt near 410 km, postulated [Bercovici and Karato, 2003] and recently reported to be observed below the western US [Song *et al.*, 2004]. However, Demouchy *et al.* [2005] show that although H₂O contents can exceed 2.2 % by weight in wadsleyite at 900°C, water contents at 1400°C on a more realistic geotherm would be less than one percent, similar to what is observed in forsterite at 1250°C at 12GPa [Mosenfelder *et al.*, 2006, Smyth *et al.*, 2006]. At water contents of 2000 to 5000 ppmw, a small amount of partial melt would not occur near 410 km, but might occur near the low velocity zone [Smyth *et al.*, 2006; Mierdel *et al.*, 2006]. Water contents of mid-ocean ridge basalts at 1000 to 2500 ppmw would appear to be inconsistent with such a high water contents in the upper mantle. However, mid-ocean ridge basalts might not be representative of ocean crustal magmatism, but rather

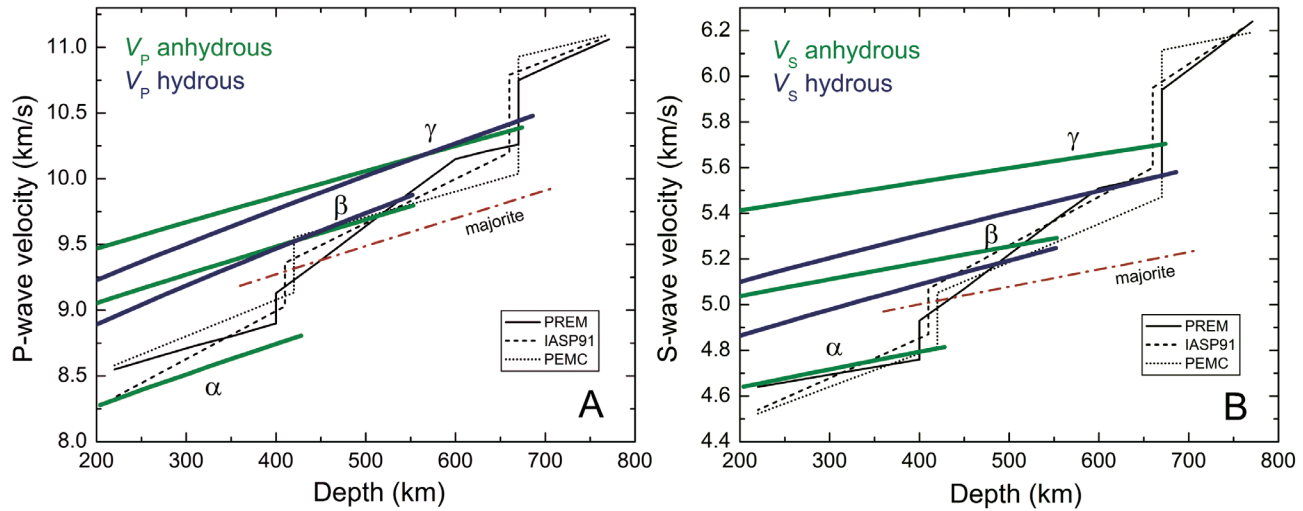


Plate 1. The effect of water on seismic velocities in Earth's Transition Zone (TZ), 410–660 km depth. Plot of monomineralic P-wave velocities (A) and shear velocities (B) versus depth for anhydrous (green) and hydrous (~1 wt% H₂O, blue) phases of wadsleyite (β), and ringwoodite (γ) using assumed thermoelastic parameters given in Table 1 and finite strain equations of state along an adiabat with 1673 K foot temperature. Velocities for anhydrous olivine (α) and majorite are also shown (see text for details). For comparison, several seismic velocity models are also shown. The figure illustrates that effect of water, which is to reduce elastic moduli, but elevate their pressure derivatives. The difference between anhydrous and hydrous P-wave velocities diminishes in the transition zone, whereas hydrous S-wave velocities remain several percent lower than anhydrous velocities throughout the TZ. Therefore, low S-wave velocities along with elevated V_p/V_s ratios would be indicative of a hydrous transition zone.

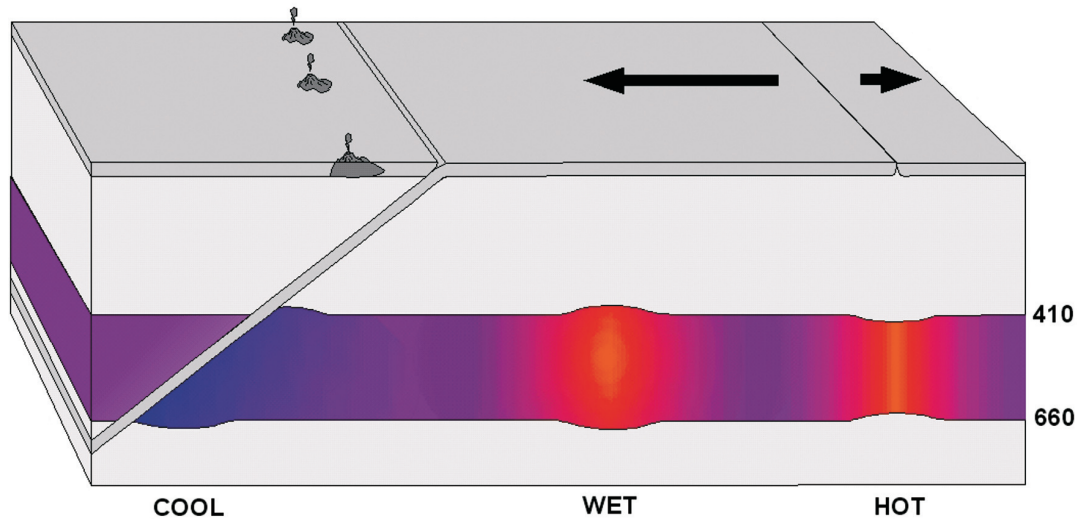


Plate 2. A schematic drawing of the contrasting effects of hot upwelling (right), hydrous (center), and a cold, subducting (left) regions of the Transition Zone, where blue indicates seismically fast and red indicates slow regions. A shallow 410 and deep 660 with intervening low S-wave velocities and elevated V_p/V_s ratios would indicate hydrous conditions in the Transition Zone.

result from nearly dry melting in the center of the up welling convection beneath the ridge [Lee and DePaolo, 2005].

A little water goes a long way in Earth's interior because of the enormous volumes of rock involved. Even if just 0.1 wt% H₂O resides in Earth's Transition Zone as residue of differentiation or has been later carried into the TZ in the basaltic crustal portion of the subducting lithosphere, the amount of H₂O between 410 and 660 km depth would be equivalent to almost one kilometer of liquid water on the surface. This amount seems to be a lower limit, and it is likely that fluxes are several times this amount. Geochemically, hydrogen at low pressure behaves as an incompatible element, but there is strong evidence that above 10 GPa the hydroxyl anion is a considerably more compatible species with two protons substituting for Mg in octahedral coordination. Because the proton does not occupy the position of the cation for which it substitutes in the crystal structure, H does not behave geochemically like other incompatible lithophile elements [Smyth et al., 2006]. In particular, H solubility in nominally anhydrous is much more strongly affected by pressure than that of other incompatible elements. Does the amount of liquid water on Earth's surface reflect a dynamic equilibrium with a deeper reservoir in Earth's interior? The question is now finally a major focus of interdisciplinary studies bridging mineral physics, seismology and geochemistry. We are only now beginning to gain a quantitative handle on the effects of hydration on the thermoelastic properties of the dense silicate minerals of Earth's interior.

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