Seismological Constraints on Earth's Deep Water Cycle

Suzan van der Lee

Department of Geological Sciences, Northwestern University, Evanston, Illinois, USA

Douglas A. Wiens

Department of Earth and Planetary Sciences, Washington University, St. Louis, Missouri, USA

Water can be present in the mantle in the form of hydrous melts, hydrous phases, or incorporated into the crystal structure of nominally anhydrous minerals of the major mantle mineralogy. The first two forms are likely in the uppermost mantle, where water solubility in major mantle minerals is low, whereas the latter form may be more important deeper in the upper mantle and transition zone. Seismological data contain unique and valuable information on the amount and distribution of water in the Earth's mantle. It is, however, challenging to extract this information because of limitations in the amount and density of available seismic data, multiple interpretations of similar observations, and limited quantification of the effects of water and other parameters on the seismic properties. While increased water content and elevated temperatures both lower seismic velocities, they have opposing effects on the depths of the discontinuities that bound the transition zone. And, while they both increase attenuation, they have opposing effects on the sharpness of these discontinuities. Independent geophysical observations, such a gravity, electrical conductivity, and surface heat flow, can further help to discriminate between temperature, water, and other compositional anomalies as the cause of observed seismic heterogeneity. Various types of observations have been combined to infer water content in the mantle, ranging from a few hundredths of weight percent to several weight percent. Altogether, the seismological literature suggests that the mantle is heterogeneously hydrated. However, with the limited studies available, there does not appear to be an obvious correlation between present tectonic environment and water content, though the literature shows a tendency to interpret inferred anomalously hydrous regions in the mid mantle as being related in one way or another to past subduction of oceanic lithosphere.

1. INTRODUCTION

The Earth's bulk composition of lithophile, siderophile, and chalcophile elements and its state of differentiation are fairly well understood from cosmo- and geochemistry, as well as geophysics. The Earth's mantle consists primarily of magnesium and iron silicates, with the olivine-wadsleyite-ringwoodite mineralogy comprising about half of the mantle assemblage in the top 660 km.

In contrast, the bulk water content of and its distribution within Earth is virtually unknown because of the high volatility of water. It is possible that the equivalent of several

Earth's Deep Water Cycle
Geophysical Monograph Series 168

10.1029/168GM03

ocean masses of water resides within mantle minerals, most prominently in the transition zone [e.g. *Smyth and Jacobsen*, this volume], though some argue that the solid Earth has effectively differentiated its water to the crust, hydro- and atmosphere [e.g. *Rüpke et al.*, this volume].

If an amount of water equal to that in the Pacific Ocean were homogeneously distributed over lattice defects in transition zone minerals wadsleyite and ringwoodite, the transition zone's water content would be around 0.2 wt % (i.e. 2000 ppm H_2O by weight). As shown by numerous papers in this volume, an amount of water as small as a few tenths of wt % in the Earth's mantle can significantly affect the bulk and shear moduli, density, electrical and thermal conductivity, anelasticity, anisotropy, and phase/state of mantle minerals. With the exception of thermal and electrical conductivity, all of these properties are most directly and accurately assessed through studies of seismic wave propagation.

Seismic wave propagation, however, is also affected by temperature, pressure, composition, structure, and mineralogy. In the upper third of Earth's mantle, first-order changes in seismic velocities are a gradual increase of seismic velocity with increasing pressure (depth), and sudden increases at the top and bottom of the transition zone near depths of about 410 and 660 km, which result from phase transitions in the olivine component of mantle mineralogy. Near 410 km, olivine transforms into wadsleyite, which transitions to ringwoodite over a broader depth range in the mid transition zone. Near 660 km ringwoodite transforms into the lower-mantle assemblage of perovskite and ferropericlase. Second order changes in seismic velocity and attenuation also occur laterally, under the predominant influence of lateral variations in mantle temperature, phase transitions in secondary mantle minerals such as garnet and pyroxene, variations in grain size, and compositional heterogeneity. Hydrogen from water is thus far the most important compositional factor governing the seismic and rheological properties of its host material [*Karato*, this volume; *Shito et al.*, this volume; *Jacobsen and Smyth*, this volume].

Water has a profound influence on the rheology of the upper mantle [*Hirth and Kohlstedt*, 1996; *Karato and Jung*, 1998, *Mei and Kohlstedt*, 2000a, 2000b, *Karato*, this volume]. Thus, the amount of water that resides in or cycles through the Earth's interior is an important consideration for understanding Earth's early evolution, the initiation and longevity of plate tectonics, low-velocity zones beneath oceans, and the lithospheric roots of Precambrian cratons, for example. In this chapter we review the ways in which seismology can constrain the water contents of the Earth's mantle. Two of the largest challenges that seismologists face are 1) extracting robust inferences from limited amounts of data, and 2) to discriminate the effects of water from the effects that temperature, composition, and mineralogy have on these properties.

Lateral temperature variations are widely thought to provide the largest contribution to upper mantle seismic velocity and attenuation variations, as the temperature derivatives of these quantities are non-linear and become large at high temperatures and low (uppermost mantle) pressures [*Jackson et al.*, 2002; *Cammarano et al.*, 2003]. Observational studies typically confirm this thermal dominance on seismic heterogeneity [e.g. *Goes and Van der Lee*, 2002; *Priestley and McKenzie*, 2006; *Wiens et al.* 2006b]. Water may provide the next-largest contribution. In this paper we discuss the effects of water on deep seismic structure.

2. THE EFFECTS OF WATER AND OTHER VARIABLES ON SEISMIC PROPERTIES

2.1 The Effects of Composition Other Than Water

Early research focused on the influence of iron because of its relative abundance in the mantle's magnesium silicates. In a solid-molten mantle mixture iron readily partitions into the melt [*Jordan*, 1988] and lateral variations in mantle iron content should be a fairly straightforward phenomenon if the mantle underwent varying degrees of partial melting. Initially, the effects of iron on the seismic velocity of shear waves (S velocity) were thought to be considerable [*Jordan*, 1988]. A survey of the seismic properties of upper mantle xenoliths shows a small dependence of the S velocity on iron content (0.3% per Mg number in olivine) [*Lee*, 2003]. Recent calculations suggest that the effects of melt depletion on *S* velocity are even smaller and negligible for realistic degrees of iron depletion compared to the effects of realistic variations in temperature [*Cammarano et al.*, 2003; *Schutt and Lesher*, 2006; *Matsukage et al.*, 2005], especially in the garnet lherzolite stability field. This is mostly because melting-related iron depletion in mantle olivine is accompanied by a loss of relatively Si-poor garnet, which is seismically fast [*Schutt and Lesher*, 2006]. Even the S-velocity dependence found by *Lee* [2003] suggests that realistic changes in iron for upper mantle rocks can produce only a 1–2% change in S-velocity, much smaller than expected from temperature variations.

For deeper levels in the upper mantle, data on the effects of Fe content exist for only the olivine component. These effects are considerable at transition zone depths [*Sinogeikin et al.*, 2001], but not quite as dramatic as the effects of hydrogen content [*Jacobsen and Smyth*, this volume; *Shito et al.*, this volume]. However, if ferric iron (Fe^{3+}) is abundant at such depths, Fe might have more dramatic effects on seismic properties, comparable to those of H [*Frost*, 2003].

Little is known about the influence of other minor elements in the mantle such as Al, Ca, and Na. Recent experimental work shows that the presence of ~5 wt % Al_2O_3 in perovskite reduces the shear modulus by about 6 %, but has no discernable effect on the bulk modulus [*Jackson et al.*, 2004]. The presence of Al might also affect the solubility of water in mantle phases [e.g. *Rauch and Keppler*, 2002; *Bolfan-Casanova et al.*, this volume]. Furthermore, calcium-silicate perovskite ($CaSiO_3$) probably exists in the lower mantle as a minor but separate phase, with a shear modulus 25 to 40 % below that of $(Mg,Fe)SiO_3$ perovskite [e.g. *Li et al.*, 2006; *Sinelnikov et al.*, 1998]. Carbon, like H, is a volatile element whose presence in the upper mantle is evidenced by CO_2 degassing at mid-ocean ridges, CO_2-rich magmas such as carbonatites and kimberlites, and diamond-bearing xenoliths. Recent experimental work supports carbon recycling to as deep as 300 km [*Hammouda*, 2003] or deeper [*Dasgupta et al.*, 2004], though the solubility of C into major mantle minerals such as olivine is exceptionally low (about 1 ppm) [*Keppler et al.*, 2003]. Thus, H-accommodating minerals appear more stable in the upper mantle than C-accommodating minerals, allowing a water cycle in the mantle to extend much deeper than a carbon cycle.

2.2 *The Effects of Water*

Hydrogen, or water, has emerged as one of the most influential mantle elements in terms of seismic properties. While the major-element (Si, Mg, Fe, O) composition of the mantle is relatively well constrained, its hydrogen content is much more speculative. The presence of hydrogen in mantle minerals directly affects seismic properties, as discussed, but also affects these properties indirectly by catalyzing mantle melting under particular pressure-temperature and kinematic conditions [*Eiler*, 2004; *Karato et al.*, this volume; *Revenaugh and Sipkin*, 1994]. In some regions of the mantle, such as the wedges between subducting oceanic plates and the lithosphere of the overriding plate, the presence of water has been corroborated through the analysis of rock samples erupted from arc volcanoes [*Morris et al.*, 1990; *Gaetani and Grove*, 1998; *Dixon et al.*, 2004].

Small amounts of water in mid-ocean ridge magmas suggest a modest water content of about 0.005–0.02 wt % for the MORB source [*Saal et al.*, 2002]; levels as high as 0.17 wt % are inferred for magmas erupted at back-arc spreading centers near slabs [*Kelley et al.*, 2006]. For deeper levels in the mantle we do not have such corroborating material and claims of water in the mantle from seismic data are mostly arrived at by excluding other known factors that influence seismic properties, such as temperature or Fe heterogeneity [e.g. *Nolet and Zielhuis*, 1994].

The effects of water content and possibly associated fluid-rich melts on seismic observables in the upper mantle are incompletely understood. Free water may be present in a few extremely hydrous regions of the upper mantle such as the mantle wedge immediately above a slab [*Iwamori*, 1998; *Cagniocle et al.*, 2006]. In this case the effect of free water can be calculated using a similar poroelastic calculation, which depends on the geometry of the fluid pores [*Takei*, 2002]. However, in most cases the large water contents in excess of the water solubility in upper mantle minerals will instead produce a fluid-rich melt [*Hirschmann et al.*, 2005]. The effect of melt can result from both a poroelastic effect [*Mavko*, 1980; *Hammond and Humphreys*, 2000; *Takei*, 2002] and a grain-boundary sliding mechanism [*Faul et al.*, 2004]. The effects of melt are difficult to constrain since the poroelastic effect depends on the melt geometry and the effect of the grain-boundary sliding mechanism on the shear modulus is incompletely characterized at the present time.

For most of the upper mantle, water concentrations are low enough or pressure high enough that the water is accommodated in the mineral structure of nominally anhydrous major mantle minerals, primarily olivine and pyroxene [*Hirschmann et al.*, 2005] or, in particularly cool regions such as subducting lithospheric plates, in dense hydrous magnesium silicates [*Komabayashi*, this volume]. Although little known, the effects of water incorporated in the olivine crystal structure at uppermost mantle depths are likely reduction of elastic moduli. Recent compressibility studies show that the bulk modulus of forsterite is reduced by about 6% in the presence of 0.8 wt% H_2O [*Smyth et al.*, 2005; *Smyth and Jacobsen*, this volume]. *Karato* [2003] estimated the indirect velocity reduction induced by water using the assumption that water lowers the seismic velocity through the dispersion effect of attenuation, and that the micro-creep associated with anelasticity is proportional to the macroscopic creep inferred from rheological experiments. This result suggests that water should lower the S velocity (Vs), and quality factor (Q), more than the P velocity (Vp). Using the relationships in *Karato* [2003], increasing the upper mantle water content from normal MORB (0.005 wt %) to 0.15 wt % will reduce the shear velocity by about 1.5 % in the absence of melting. However, typical mantle temperatures at shallow depths are above the wet solidus and the melt triggered by 0.15 wt% of water could further lower the S velocity significantly. This suggests that variations in the water dissolved in nominally anhydrous minerals probably produce less heterogeneity than variations in temperature for the uppermost mantle, but may be more significant than other types of compositional variations. However, the relationships proposed by *Karato* [2003] rely on a number of assumptions and extrapolations, and additional relaxation mechanisms associated with water may be possible.

For the transition zone, ultrasonic experiments [*Jacobsen and Smyth*, this volume] on ringwoodite show that the unrelaxed seismic velocities can also be lowered by the incorporation of H from water into the mineral structure. *Jacobsen and Smyth* [this volume] report that 1 wt % of water in ringwoodite would reduce its Vs by over 100 m/s (~ 2 %) while having a negligible effect on Vp at transition zone pressures. Water thus has an elevating effect on the ratio of *P* velocity over *S* velocity, and thus on Poisson's ratio, of ringwoodite.

Hydrogen also has important effects on the properties of the upper mantle discontinuities, which may allow recognition of the presence of water. Thermodynamic calculations [*Wood*, 1995; *Helffrich and Wood*, 1996] as well as laboratory experiments [*Smyth and Frost*, 2002] show that under hydrous conditions, the thickness of the 410-km discontinuity can expand from the expected ~10 km for dry conditions to as much as 40 km, if water from olivine partitions tenfold into wadsleyite. However, 40 km may be an overestimate of the maximum thickness of the 410-km discontinuity because the hydrogen storage capacity of olivine relative to that of wadsleyite has probably been underestimated [*Hirschmann et al.*, 2005]. If the water content near 410 km exceeds the storage capacities of olivine and wadsleyite, the 410-km discontinuity would sharpen and carry a fluid or melt atop it [*Hirschmann et al.*, 2005; *Chen et al.*, 2002]. The thickness of the 660-km discontinuity would also increase under hydrous conditions [*Higo et al.*, 2001], but the thickening is only about a fraction of that for the 410-km discontinuity. In contrast, the 520-km discontinuity is expected to sharpen under hydrous conditions [*Inoue et al.*, 1998].

2.3 Discriminating Between the Effects of Water and Temperature

Since the first-order effects of water and temperature on seismic velocity and attenuation are of the same sign, it is necessary to discuss possible ways to discriminate between these possibilities. In principle, such discrimination is possible if the ratios of partial derivatives of the observables to their causes are not alike. For example, if the observables are Vs and Vp, we must have $(\partial Vp/\partial T)/(\partial Vs/\partial T) \neq (\partial Vp/\partial w)/(\partial Vs/\partial w)$ to allow discrimination between water content w, and temperature T. Here we consider the effects of temperature and water content anomalies on the mid and upper mantle. The dependence of seismic velocities on water and temperature is non-linear because at high water content or high temperature, attenuation is stronger, which amplifies the effects of small perturbations in temperature and water content on seismic velocities relative to their effects at lower temperature and lower water content [*Karato*, 2003, 2006; *Jackson et al.*, 1992]. Thus while the values of the partial derivatives, and thus the contrast between them, depends on the actual temperature and water content, the following examples are nonetheless representative, in terms of their potential for discrimination, for a fair range of temperatures and water content.

If the mantle temperature at a depth of 600 km is elevated by 400 °C, the S- and P-velocities would be lowered by approximately 2.8 and 1.8 %, respectively [*Cammarano et al.*, 2003], which includes the effects of thermal expansion (anharmonic term) and increased attenuation (anelastic term). Water content elevated by 1 wt % in ringwoodite lowers ultrasonic S- and P-velocities by about 2.4 % and a negligible amount, respectively [*Jacobsen et al.*, 2004; *Jacobsen and Smyth*, this volume]. Actual S- and P-velocities (at seismic frequencies) would be further lowered by an anelastic effect of roughly 3 and 1.5 %, respectively [*Karato*, 2006]. Thus, the ratio of the P to S-velocity of a wet transition zone mantle would increase by several percent more than that for a hot transition-zone mantle. However, a temperature anomaly of 400 °C would depress the 410-km discontinuity by 30 to 50 km [*Litasov et al.*, this volume], elevate the 660-km discontinuity by an amount between 7 and 40 km [*Litasov et al.*, this volume], and thus reduce the transition thickness. In contrast, the wet mantle would thicken the transition-zone through elevation of the 410 km discontinuity up to anywhere from 10 to 30 km [*Smyth and Frost*, 2002; *Hirschmann et al.*, 2005] and depression of the 660-km discontinuity by up to 4 km [*Higo et al.*, 2001]. Furthermore, in a wet mantle these discontinuities would broaden, with widths of up to 40 km for the 410 km [*Smyth and Frost*, 2002; *Hirschmann et al.*, 2005] and up to 8 km for the 660 km discontinuity [*Higo et al.*, 2001], while in a hot mantle these discontinuities, in particular the 410-km discontinuity, would sharpen by around 5 km [*Helffrich and Bina*, 1994]. Thus it appears that for the transition zone, the effects of temperature and water can be distinguished by the different Vp/Vs ratios of the anomalies and by their differing effects on the mantle discontinuities.

At a depth of 100 km and 1250 °C, a 400 °C temperature increase would lower the S- and P-velocity by about 9 and 6 %, respectively [*Jackson et al.*, 2002; *Faul and Jackson*, 2005]. The effect of water on upper mantle velocities has not been fully established. Because water significantly lowers the bulk modulus of forsterite [*Smyth et al.*, 2005; *Smyth and Jacobsen*, this volume], we expect its shear modulus to be lowered as well. Temporarily assuming the effect of water on ringwoodite velocities at room pressure [Jacobsen et al., 2004] for olivine yields S and P velocities that are 1.8 and 1% lower, respectively, in the presence of 0.2 wt % of water. *Karato* [2003] estimated the additional effects of water on seismic velocities through shear modulus anelasticity, which suggests changes of 1.7% and 0.8% for Vs and Vp respectively for a water content of 0.2 wt % in the mantle, which is about the maximum water content that could be incorporated without producing hydrous melting [*Hirschmann et al.*, 2005]. Altogether 0.2 wt % of water might lower Vs and Vp by 3.5 and 1.8 %, respectively. Thus, for the uppermost mantle, limitations on the amount of water that can be taken up in mantle minerals suggest that the effects of water heterogeneity on seismic velocities and attenuation will be less than the effects of temperature variations, unless hydrous minerals or a hydrous melt is produced.

It may be possible to use the relationship between Vp, Vs, and anelasticity (1/Q) to distinguish temperature and water effects in the upper mantle, since attenuation depends linearly on water content but exponentially on the temperature anomaly [*Karato*, 2006]. The effect of water on olivine will produce a larger percentage change in Vs than in Vp when compared to the temperature effect, particularly at lower temperatures where the anelastic effect of temperature is minor. This suggests that the relationship between Vp, Vs, and Q can be used to distinguish water from temperature in the upper mantle [*Karato*, 2003; *Shito et al.*, this volume]. However, the differences between $(\partial Vp/\partial T)/(\partial Vs/\partial T)$ and $(\partial Vp/\partial w)/(\partial Vs/\partial w)$ are probably reduced at high temperatures in the upper mantle, where the temperature effects also reflect a large anelastic effect.

To discriminate seismologically between water content and temperature it thus appears most instructive in general to study S velocities along with P velocities and Q, as well as properties of mantle discontinuities. For the uppermost mantle, additional data such as surface heat flow, gravity, and the water content of erupted mantle basalts and xenoliths may be helpful in discriminating between different effects. Surface heat flow would be elevated for a thermal anomaly but not for a hydration anomaly. Likewise, gravity may provide constraints since a 400 °C thermal anomaly would lower the density by 1.8%, whereas a few tenths of wt % water taken up in the crystal structure of mantle minerals will have a negligible effect on gravity.

A definitive interpretation of tomographic images alone in terms of temperature, water content, and, in the shallow mantle, melt, are limited by incomplete data and understanding of the effects of melt and water, and to some extent temperature on seismic velocities and attenuation. Another limiting factor is the low resolution of and non-uniqueness in the seismic images or differences in resolution between Vs, Vp, and Q images. However, spatial coherence, depths and sharpness of seismic discontinuities, surface heat flow, density, and estimates of electrical conductivity can help favor one interpretation over another. Interpreting the seismic results in the context of known and publicly available surface heat flow and gravity data, as well as published xenolith analyses, would greatly enhance the potential of the seismological data for assessing the hydration state of the mantle.

3. SEISMOLOGICAL CONSTRAINTS ON MANTLE WATER CONTENT

Seismic clues that could point to the presence of water in the mantle include lowered seismic velocities, elevated or depressed discontinuities, broadened or sharpened discontinuities, enhanced attenuation, and unconventional anisotropy patterns. On their own, each of these clues can be explained with alternatives to hydrogen, such as heightened or lowered temperatures, but in combination with each other and/or in a context provided by non-seismic data the clues can make a strong case for the presence of hydrogen/water in the mantle.

3.1 The Mantle Wedge

The mantle wedge, lying above the partially-hydrated oceanic crust of the downgoing slab, undoubtably receives the largest water input of any mantle region, and probably represents the most hydrated part of the upper mantle. This is perhaps the only part of the mantle in which substantial water may be present in three fundamental forms: as a free fluid [*Iwamori*, 1998], incorporated in hydrous minerals [*Davies and Stevenson*, 1992], and dissolved in nominally anhydrous minerals like olivine and pyroxene [*Kohlstedt et al.*, 1996]. Dehydration of the slab and fluxing of the mantle wedge is responsible for most island arc volcanism, as demonstrated by the predominance of fluid mobile elements in island arc volcanics [*Morris et al., 1990; Plank and Langmuir*, 1993; *Tatsumi and Eggins*, 1995].

The distribution of water within the mantle wedge is highly uncertain. It is well established that the downgoing slab releases water into the wedge beneath the island arc, which generally occurs where the slab depth is between 90–130 km [*England et al.*, 2004], but several different mineralogical reactions are involved in the dehydration [*Schmidt and Poli*, 1998]. Several subduction zones show distinct low velocity crustal layers that decrease in amplitude near 120–150 km depth, probably due to dehydration and eclogitization reactions in the subducting crust [*Yuan et al.*, 2000; *Ferris et al.*, 2003]. It is still unclear how much the slab releases of its water in the island arc region, and how much it retains and releases deeper in the mantle. This question has major implications for the amount and distribution of water in the deeper mantle.

The occurrence of water and fluid-mobile elements in various arc and backarc volcanics provide some clue about the distribution of water within the mantle wedge. Backarc spreading centers, which sample the mantle wedge, show decreasing levels of water and fluid mobile elements with increasing distance into the backarc, reaching levels typical of nominally dry mantle (MORB) at several hundred kilometers distance from the arc [*Pearce et al.*, 1995; *Taylor and Martinez*, 2003; *Kelley et al.*, 2005]. This evidence suggests that water is concentrated near the subducted slab and does not permeate the entire mantle wedge into the far backarc, at least at shallow (< 100 km) depths. In some cases, however, the mantle can be found hydrated many hundreds of km away from the slab if the slab's dip angle recently steepened, such as in the central Andes [*Kay et al., 1999; James and Sacks, 1999*].

Seismology has the potential of resolving many of the questions about water in the mantle wedge. Most seismic tomographic models of arcs show an inclined region of low Vp and Vs about 50 km above the slab, extending from the backarc to beneath the volcanic front [*Zhao et al.*, 1992; *Zhao et al.*, 1995; *Nakajima et al.*, 2001]. Larger-scale tomographic models show low seismic velocities and high attenuation throughout a large region of the mantle wedge, occasionally extending many hundreds of kilometers into the backarc [*Zhao et al.*, 1997; *Van der Lee et al.*, 2001, 2002; *Conder and Wiens*, 2006] (Plates 1 and 2). The prominent low-velocity anomaly in Plate 1 characterizes the mantle wedge beneath the central Andes and above the Nazca slab. The strength and spatial isolation of the anomaly have lead to it being interpreted as a relatively water- and melt-rich rather than a hot zone [*Van der Lee et al.*, 2001, 2002]. On the other hand, *Wiens et al.* [2006b] find that for various backarc spreading centers the lowest seismic velocities correlate well with petrological indicators of mantle temperature and fails to correlate with petrological estimates of mantle water content [*Kelley et al.*, 2006], suggesting that the seismic anomalies in backarcs may be largely controlled by temperature variations and not by water content.

In the upper 100–150 km beneath the arc and backarc, large seismic velocity and attenuation anomalies (Plate 2) have variously been interpreted as the effects of temperature, melt, and water. The effect of temperature on seismic velocities and attenuation are non-linear in the upper mantle, such that the effects become large at higher temperatures (1200–1400 °C) [*Jackson, et al.*, 1992; *Karato*, 1993; *Jackson, et al.*, 2002]. Furthermore, the seismic anomalies are also a function of grain size [*Jackson, et al.*, 2002; *Faul and Jackson*, 2005]. However, the large magnitude of the velocity and attenuation anomalies in the mantle wedge suggests that temperature effects alone cannot be entirely responsible, and that water and/or melt provide an important effect [*Conder and Wiens*, 2006; *Wiens et al.*, 2006a; *Van der Lee et al.*, 2000; 2001].

3.2 Upper Mantle Below the Mantle Wedge, Including the Transition Zone

Much less is known about the presence, cycling, and role of water in the mantle below the mantle wedge. This is in part because these mantle depths are not nearly as well sampled by magmatism and for another part because typical earthquake-seismometer distributions allow for higher resolution in imaging mantle wedge structure than in imaging deeper parts of the mantle.

Nevertheless, seismologists have imaged deep seismic anomalies that are unlikely results of temperature, iron, or grain size anomalies and thus more likely the result of water. As the solubility of water in olivine increases strongly with depth [*Kohlstedt, et al.*, 1996; *Chen et al.*, 2002; *Mosenfelder et al.*, this volume; *Hirschmann et al.*, this volume], water at depths below the mantle wedge would likely be absorbed into the olivine crystal structure, and would cause increased attenuation, lower seismic velocities, thickened transition zone, as well as broadened 410- and 660-km phase transitions. For example, *Nolet and Zielhuis* [1994] argued that a low S-velocity anomaly near depths of 300 km was caused by water enrichment of formerly depleted tectosphere by ruling out other known explanations for S-velocity anomalies. *Revenaugh and Sipkin* [1994] interpreted a low-velocity layer atop the 410-km discontinuity as an accumulation of melt from water-triggered melting of the deep upper mantle. *Zhao et al.* [1997] suggested that low P velocities extending to depths of 400 km in Tonga-Fiji likely result from the presence of water. The nearby subducting slab was implicated as the source of the water, though it is unclear whether the water-containing minerals in the slab would dehydrate at these depths or the water or water-rich mantle might have migrated up to these depths after having formed from slab dehydration near or in the lower mantle. A more recent analysis shows that these large low-velocity anomalies extend to only 250-300 km depth in Tonga-Fiji [*Conder and Wiens*, 2006] (Plate 2). However, *Shito and Shibutani* [2003] found high attenuation at depths between 200–400 km beneath the Philippine Sea and also suggested this may result from water from the subducting Pacific slab [*Shito et al.*, this volume].

Assuming that subducting slabs remain somewhat hydrous after passage through the mantle wedge above 150 km, *Komabayashi* [this volume] shows that dehydration reactions between 150 and 600 km are atypical and occur only in special circumstances. For example, if a slab flattens in the transition zone, it would eventually be warm enough for the dense hydrous magnesium silicates it might contain to break down and release water to the overlying upper mantle. This intermediate-depth dehydration could explain the low-velocities imaged by *Zhao* [2004] in the upper 400 km beneath

China, right above the Pacific slab, which appears to lie flat in the transition zone here. *Zhao* [2004] proposes that intraplate volcanism at the Chinese Wudalianchi and Changbai volcanoes is a result of this hydrated mantle. Cold slabs that do not heat up sufficiently in the transition zone would not dehydrate until they reached depths near the bottom of the transition zone or top of the lower mantle [*Komabayashi*, this volume]. *Van der Lee et al.* [2006] propose that the overlying mantle hydrated by the dehydrating slab might form a slow upwelling and eventually interact with lithosphere at the surface. Such a deep hydrous upwelling would have low S velocities, as imaged above the Farallon Plate beneath the eastern US (Plate 3). Subduction-induced deep hydrous upwellings could be related to intraplate volcanism and at a continent-ocean transition it could initiate a new subduction zone [*Van der Lee et al.*, 2006], thus implying that an advanced subduction process can eventually trigger a new subduction zone because of this deep water cycle.

Most of these inferences for hydrous material in the upper mantle are based on low seismic-velocity or low-Q anomalies. However, low velocities and low Q can have alternative explanations, such as elevated temperatures. Reasons for the mentioned studies to preferentially explain the observations with the presence of water are based upon the exclusion of other potential explanations and could thus change if this potential were expanded. These reasons range from the anomalies being close to a subducting slab and its associated volcanism [*Zhao*, 2004; *Shito and Shibutani*, 2003; *Conder and Wiens*, 2006], incomplete consistency of temperatures inferred from co-located S, P and Q anomalies [*Conder and Wiens*, 2006], the anomalies being so slow that only unrealistic temperature elevations or iron enrichment can explain them [*Nolet and Zielhuis*, 1994; *Revenaugh and Sipkin*, 1994; *Van der Lee and Nolet*, 1997], the absence of a hot source and of elevated heat flow as well as the properties of transition zone seismic discontinuities [*Van der Lee et al.*, 2006].

In fact, the properties of transition zone discontinuities themselves have been cited as primary evidence for a wet, as well as for a dry mantle. For example, *Courtier and Revenaugh* [this volume] infer water deep beneath the eastern US from their observing an elevated 410-km discontinuity and anomalously strong 520-km discontinuity. This is consistent with low S velocities imaged here by *Van der Lee and Nolet* [1997]. *Van der Meijde et al.*'s [2003] observations of a broadened 410-km discontinuity imply about 0.05–0.09 wt % or more [*Hirschmann et al.*, 2005] of water in olivine around depths of 410 km beneath parts of the Mediterranean region (Figure 1). The transition zone beneath this region is densely populated by recently subducted slab fragments [*Marone et al.*, 2004], which could be a likely source for the water but are not sufficiently cold to explain the observed broadened discontinuity. *Blum and Shen* [2004] also argue that an elevated 410-km discontinuity beneath southern Africa cannot be solely explained by lowered temperatures inferred from seismic tomography [*James et al.*, 2001] and infer that part of the uplift is caused by 0.3 to 0.7 wt % of water in the transition zone. *Suetsugu et al.* [this volume] infer about 1.2 ± 0.2 wt % of water in the bottom of the transition zone from tomographically imaged relatively normal *P* velocities and a depressed 660-km discontinuity. *Song and Helmberger* [this volume] deduced a layer of low velocities atop the 410-km discontinuity beneath the western US. This low-velocity layer might be caused by water released by the subducted Farallon Plate, although the expected melt layer [*Hirschmann et al.*, this volume] would be significantly thinner than that inferred by *Song and Helmberger* [this volume].

In contrast, *Gilbert et al.* [2003] imply that a lack of correlation between discontinuity width and uplift beneath the western US suggests that water does not play a dominant role there. A review of discontinuity widths and depths worldwide by *Helffrich* [2000] suggests that the seismologically inferred sharpness of the 410-km discontinuity precludes the transition zone from being extensively hydrated. *Tibi and Wiens* [2005] and *Braunmiller et al.* [this volume] investigated discontinuities in active subduction zones (Tonga and Andes, respectively) and found that their characteristics are consistent with a dry transition zone. Independently from the seismological evidence, *Dixon et al.* [2002] use geochemical analyses of volcanic rocks to argue that little surface water is subducted into the deep upper mantle.

4. DISCUSSION

Seismic observations have inferred [*Suetsugu et al.*, this volume; *Song and Helmberger*, this volume; *Zhao et al.*, 1997; *Shito et al.*, this volume; *Van der Meijde et al.*, 2003] and excluded [*Tibi and Wiens*, 2005; *Gilbert et al.*, 2003] water in the deep upper mantle next to or near subducting slabs. Away from slabs, inferences on water content of the mantle also vary [*Blum and Shen*, 2004; *Gao et al.*, 2002; *Chambers et al.*, 2005; *Shearer and Flanagan*, 1999; *Helffrich*, 2000]. Differences between these studies are in 1) the region studied, 2) the data analyzed, and 3) the way the data were processed. It is quite possible that there are regional differences between subducting slabs, in terms of their level of hydration, their temperatures at depth, and associated dehydration reactions. Some slabs may not carry much water downwards from the mantle wedge, others could dehydrate upon flattening and associated warming in the transition zone, while yet others would not dehydrate until reaching the lower mantle [*Komabayashi*, this volume]. It is also possible that different data highlight different aspects

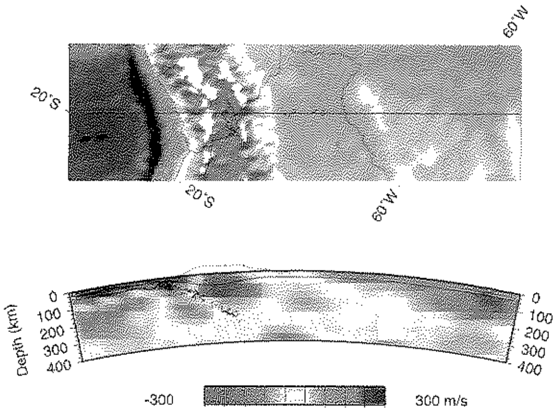

Plate 1. Cross section through South America showing large-scale anomalous S-velocity structure and Moho depth, jointly inferred from regional S and surface wave forms, receiver functions, and surface wave group velocities. The tomographic model is from *Feng et al.* [submitted manuscript]. The grey dots are earthquake hypoconeters.

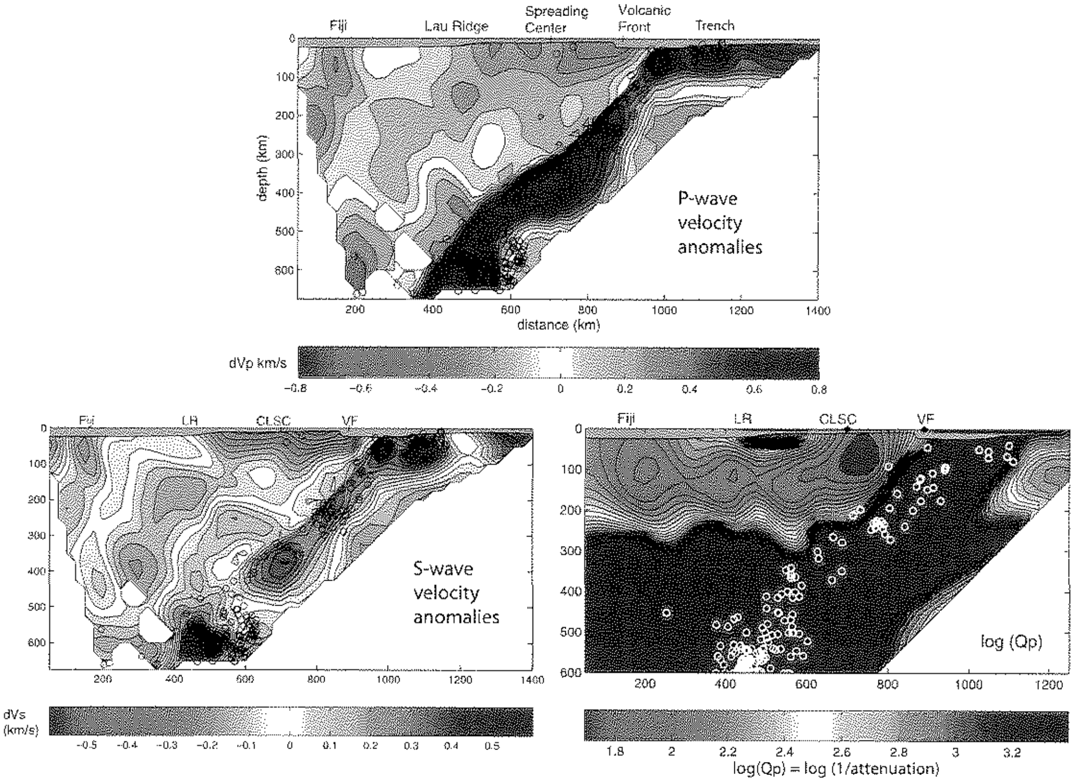

Plate 2. P, S, and Q images of the Tonga subduction zone and Lau backarc basin. VF denotes the Tonga volcanic front, CLSC denotes the Central Lau Spreading Center, and LR denotes the Lau Ridge (relict arc). Note that P and S images show anomalies relative to an average model, whereas the attenuation image shows log(Q) without a reference model. Low seismic velocities and low Q extending to depths of 250–300 km may result from water in the mantle wedge. P and S wave images are from *Conder and Wiens* [2006]; Q structure is re-inverted from data in *Roth et al.*, [1999].

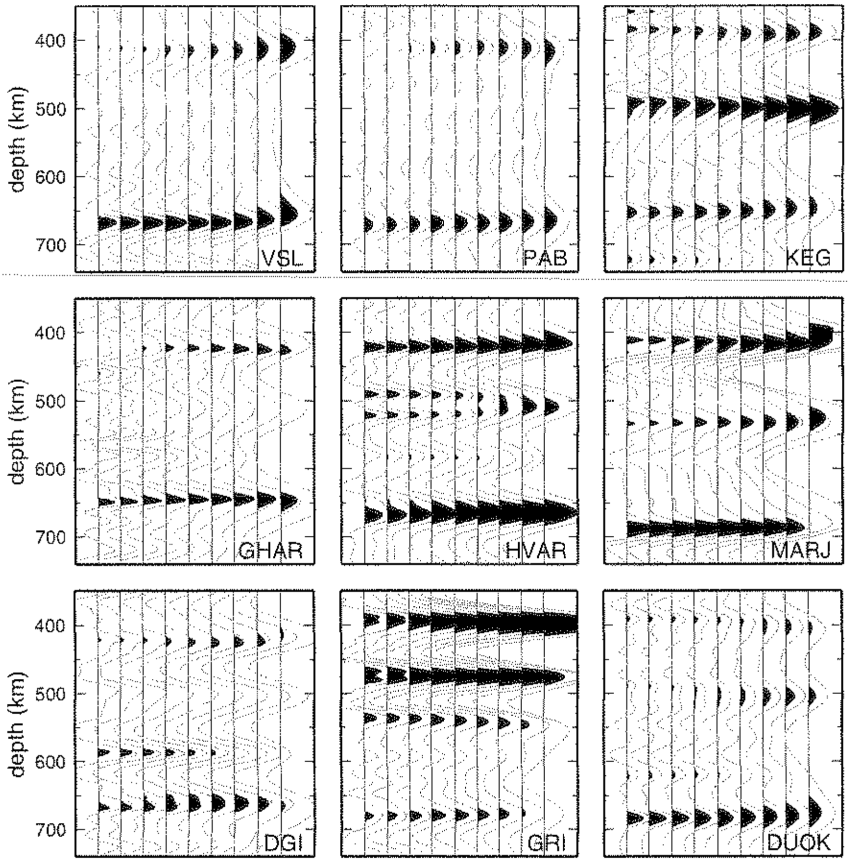

Figure 1. Receiver functions (grey lines) from *Van der Meijde et al.* [2003]. Positive signals are filled with black wherever they are significantly larger than zero with more than 95 % confidence. Black fill reaches to 2 standard deviations below the signal. Seismic stations are from the MIDSEA network [*Van der Lee et al.*, 2001]. Multiple receiver functions for each station represent a decreasing low-pass frequency from left to right. The positive signal (indicating a *P* to *S* conversion) generated by the 410-km discontinuity gets stronger with decreasing frequency, which is not observed to the same extent for discontinuities at other depths. This frequency-dependence indicates that the 410-km phase transition occurs over larger than standard depth intervals, which in turn could point to the presence of water in this depth region, which is known to significantly broaden the olivine to wadsleyite transition interval in water-undersaturated conditions [*Wood*, 1995; *Smyth and Frost*, 2002; *Hirschmann et al.*, this volume; *Karato*, 2006b]. The inferred widths of over 20 km could imply between 0.05 [*Wood*, 1995] and 0.2 [*Hirschmann et al.*, this volume] wt % of water in olivine near 410 km.

of the mantle. For example, receiver functions [*Gilbert et al.*, 2003] would record a water-triggered low-velocity layer on the 410 only if its top was sharply defined, while triplicated S waves would sense the layer no matter how sharp its top was [*Song and Helmberger*, this volume]. More disconcerting is that different inferences have been drawn because of different data processing methods for the same regions and very similar data sets. For example *Blum and Shen* [2004] find a transition zone beneath southern Africa that is 25 km thicker than a normal thickness of 245 km found there by *Gao et al.* [2002] from virtually the same data. The different result must be due to differences in data processing, yet the superiority of one processing method over another is not established.

Rather than inferring one type of seismic property at a time, it seems advisable to simultaneously infer several properties from a diverse data set as such would yield more mutually consistent results and subsequently more robust models of mantle water content. For example, ignored, underestimated, or spatially unresolved velocity heterogeneity in a mantle-discontinuity study can bias the inferred depths of the discontinuity. Likewise, unaccounted discontinuity relief can bias seismic-velocity models.

Water affects many physical properties of the mantle, including the thickness of phase transitions. Studies of long-wavelength seismic waves, such as *SS* precursors, would record lower impedance contrasts for thicker phase transitions. On a global scale, *Chambers et al.* [2005] used such waves to map the impedance contrast at the 410-km discontinuity to be about 30 % lower than that found by *Shearer and Flanagan* [1999] from a somewhat sparser but very similar data set. Shorter-wavelength seismic waves, such as *P* to *S* converted waves or *PP* precursors, can place bounds on the thickness and sharpness of the 410-km discontinuity, as reviewed by *Helffrich* [2000]. *Helffrich* [2000] quotes maximum sharpness estimates from the literature of 4 to 5 km to support the 410-km discontinuity representing a phase change. Such a sharp discontinuity would also imply a dry mantle, as even a slightly wet mantle would thicken the phase transition [*Wood*, 1995; *Smyth and Frost*, 2002; *Karato*, 2006b]. However, the quoted 4–5 km are typically presented in the literature as the minimum thickness that would be consistent with the data analyzed. For example, *Benz and Vidale* [1993] analyzed data from two earthquakes, of which *P410P* precursors of one lead to a thickness inference of 4 km, while the other implies a much thicker 410-km discontinuity through the absence of *P410P* precursors. The data of *Neele and Snieder* [1992] as well as of *Vidale et al.* [1995] imply a thickness of 4 to 10 km, if not more, while *Yamazaki and Hirahara* [1994] show that the 410-km discontinuity must be significantly wider than 5 km. Globally, thicknesses of 4–5 km for the 410-km discontinuity thus seem more of an exception than a rule, in essence leaving it somewhat open whether the mid upper mantle is typically wet or dry.

5. OUTLOOK

Seismic data analysis provides without doubt unique and valuable ways to constrain the water content of the solid Earth. However, many challenges remain for this assessment. Some can be conquered only through collaborative cross-disciplinary research between, for example, seismologists and mineral physicists. Other challenges must be addressed by seismologists benchmarking their data processing methods and reducing the non-uniqueness of their models. Based on our review of seismologists' attempts to infer the water content of the upper mantle, we propose two different approaches that would contribute to the success of these attempts.

The first way is combining a variety of geophysical data that together can distinguish between hydrogen and other explanations. For example, a wet transition zone would be thicker and have low S velocities, while a cold transition zone would be thicker and have high S velocities. Or, a low-velocity anomaly below a region with high surface heat flow could be hot while a low-velocity anomaly under a region with low surface heat flow is more likely to be wet. Electrical conductivity provides independent information on the hydration state of at least the uppermost mantle. A steady-state situation requires smooth spatial changes due to temperature, which dissipates by nature, while abrupt spatial change is more likely compositional in origin. *Rychert et al.* [2005] used this method of discrimination to argue that the asthenosphere beneath the northeastern US is wet. A powerful approach is to simultaneously map heterogeneity in P velocity, S velocity, and anelasticity with comparable resolving power for the same region [*Conder and Wiens*, 2006; *Shito et al.*, this volume]. Water, temperature and melt have different relative effects on these properties.

A second way is for seismologists to use their data as a verification/falsification and correction tool for mineral physics models rather than independently invert their data for a regularized seismic model. For example, seismologists will use the petrologically derived seismic velocities of *Gerya et al.* [2006] as a starting model to explain their regional travel-time data and use discrepancies to adjust the model's petrological parameters rather than velocities on a regular, but non-physical grid. For another example, models for the entire upper mantle will start from velocities based on heat-flow derived laterally-varying geotherms, then adjust the geotherm parameters where indicated by the data and explain the remaining discrepancies with compositional anomalies.

6. CONCLUSIONS

For assessing the water content of the deep Earth seismologists have some of the most powerful tools, but also face considerable challenge in 1) extracting robust inferences from limited amounts of data and 2) discriminating the effects of water from those of other mantle properties. The first challenge can be lessened by more extensive benchmarking of data processing techniques, and simultaneous rather than independent inference of various mutually consistent seismic properties. Perhaps even more important is to expand seismic data sets, in particular by acquiring data in unexplored terrain, including aseismic regions, seas, and oceans, and by widening and densifying existing seismic arrays. The second challenge can be lessened by simultaneously interpreting different types of seismic data and combining them with cross-disciplinary inferences from mineral physics and other branches of geophysics. This task is greatly facilitated when seismologists and mineral physicists communicate, as this book intends to encourage. Seismological inferences on the Earth's deep water content and cycle depend completely on mineral physicists characterizing the seismic properties of hydrated mantle minerals and assessing the impact of compositional anomalies other than hydration on those seismic properties. Lastly, we encourage mineral physicists to construct physically plausible hypothetical seismic models for the Earth's mantle that seismologists can test against seismic data.

Acknowledgements. We thank Steven Jacobsen, Guust Nolet, and Heather Watson for the promptest ever reviews. Their thoughtful, critical, and helpful comments significantly improved this chapter.

REFERENCES

Benz, H. M., and J. E. Vidale, Sharpness of upper-mantle discontinuities determined from high-frequency reflections, nature, 365, 147–150, 1993.

Blum, J., and Y. Shen, Thermal, hydrous, and mechanical states of the transition zone beneath southern Africa, Earth Planet. Sci. Lett., 217, 367–378, 2004.

Bolfan-Casanova, N., C. McCammon, and S. Mackwell, Water in transition zone and lower mantle minerals, this volume, 2006.

Braunmiller, J., S. van der Lee, and L. Doermann, Transition-zone thickness in the central South American Subduction Zone from receiver functions, this volume.

Cagnioncle, A.-M., E. M. Parmentier, and L. T. Elkins-Tanton, The effect of solid flow above a subducting slab on water distribution and melting at convergent plate boundaries, Earth Planet. Sci. Lett., in press, 2006.

Cammarano F., S. Goes, P. Vacher, and D. Giardini, Inferring upper mantle temperatures from seismic velocities, Phys. Earth Planet. Inter., 138, 197–222, 2003.

Conder, J. A., and D. A. Wiens, Seismic structure beneath the Tonga arc and Lau backarc basin determined from joint Vp, Vp/Vs tomography, Geochem. Geophys. Geosystems, 7, Q03018, doi: 10.1029/2005GC001113, 2006.

Chambers, K., A. Deuss, and J.H. Woodhouse, Reflectivity of the 410-km discontinuity from PP and SS precursors, J. Geophys. Res., 110, doi:10.1029/2004JB003345, 2005.

Chen, J., T. Inoue, H. Yurimoto, and D. J. Weidner, Effect of water on olivine-wadsleyite phase boundary in the (Mg,Fe)2SiO4 system, Geophys. Res. Lett., 29, doi:1810.1029/2001GL014429, 2002.

Dasgupta, R., M. M. Hirschmann, and A. C. Withers, Deep global cycling of carbon constrained by the solidus of anhydrous, carbonated eclogite under upper mantle conditions, Earth Planet. Sc. Lett., 227, 73–85, 2004.

Davies, J. H., and D. J. Stevenson, Physical model of source region of subduction zone volcanics, *Journal* of Geophysical Research, 97, 2037–2070, 1992.

Dixon, J. E., Leist, L., Langmuir, C., and Schilling, J. G., Recycled dehydrated lithosphere observed in plume-influenced mid-ocean ridge basalt. Nature, 420, 385–389, 2002.

Dixon, J. E., T. H. Dixon, D. Bell, R. Malservisi, Lateral variation in upper mantle viscosity: role of water, Earth and Planetary Science Letters, 222, 451–467, 2004.

Eiler, J., Inside the subduction factory, AGU Geophysical Monograph Series, 138, 324 pp., 2004.

England, P., R. Engdahl, and W. Thatcher, Systematic variation in the depths of slabs beneath arc volcanoes, *Geophysical Journal International, 156*, 377–408, 2004.

Evans, R., G. Hirth, K. Baba, D. Forsyth, A. Chave, R. Mackie, Geophysical evidence from the MELT area for compositional controls on oceanic plates, *Nature, 437*, 249–253, 2005.

Faul, U. H., J. D. Fitz Gerald, and I. Jackson, Shear wave attenuation and dispersion in melt-bearing olivine crystals: 2. Microstructural interpretation and seismological implications, *J. Geophys. Res., 109*, doi: 10.1029/2003JB002407, 2004.

Faul, U. H., and I. Jackson, The seismological signature of temperature and grain size variations in the upper mantle, *Earth Planet. Sci. Lett., 234*, 119–134, 2005.

Ferris, A., G. A. Abers, D. H. Christensen, and E. Veenstra, High resolution image of the subducted Pacific(?) plate beneath central Alaska, 214, Earth Planet. Sci. Lett., 575–588, 2003.

Frost, D. J., The structure and sharpness of $(Mg,Fe)_2SiO_4$ phase transformations in the transition zone, Earth Planet. Sci. Lett., 216, 313–328, 2003.

Gaetani, G. A., and T. L. Grove, The influence of water on melting of mantle peridotite. Contrib. Mineral. Petrol., 131, 323–346, 1998.

Gao, S. S., P. G. Silver, K. H. Liu, and the Kaapvaal Seismic Group, Mantle Discontinuities Beneath Southern Africa, Geophys. Res. Lett., 29, 10.1029/2001GL013834, 2002.

Gerya, T. V., Connolly, J. D., Yuen, D. A. , Gorczyk, W. and A. M. Capel, Seismic implications of mantle wedge plumes, Phys. Earth Planet. Inter., 156, 50–74, 2006.

Gilbert, H. J., A. F. Sheehan, K. G. Dueker, and P. Molnar, Receiver functions in the western United States, with implications for upper mantle structure and dynamics, J. Geophys. Res., 108, doi:10.1029/2001JB001194, 2003.

Goes, S., and S. van der Lee, Thermal structure of the North American uppermost mantle inferred from seismic tomography, J. Geophys. Res., 107, DOI:10.1029/2000JB000049, 2002.

Grand, S.P., Mantle shear-wave tomography and the fate of subducted slabs, Philosophical Transactions Royal Society of London, Series A, 360, 2475–2491, 2002

Hammond, W. C., and E. D. Humphreys, Upper mantle seismic wave velocity: Effects of realistic partial melt geometries, *J. Geophys. Res., 105*, 10,975–910,986, 2000.

Hammouda, T., High-pressure melting of carbonated eclogite and experimental constraints on carbon recycling and storage in the mantle, Earth Planet. Sc. Lett., 214, 357–368, 2003.

Helffrich, G. Topography of the transition zone seismic discontinuities Rev. Geophys., 38, 141–158, 2000.

Helffrich, G., and C. R. Bina, Frequency dependence of the visibility and depths of mantle seismic discontinuities, Geophys. Res. Lett., 21, 2613–2616, 1994.

Helffrich, G., and B. Wood, 410-km discontinuity sharpopness and the form of the olivine phase diagram: Resolution of apparent seismic contradictions, Geophys. J. Int., 126, F7–F12, 1996.

Higo, Y., T. Inoue, T. Irifune, and H. Yurimoto, Effect of water on the spinel-postspinel transformation in Mg_2SiO_4, Geophys. Res. Lett., 28, 3505–3508, 2001.

Hirschmann, M. M., C. Aubaud, and A. C. Withers, Storage capacity of H_2O in nominally anhydrous minerals in the upper mantle, Earth Planet. Sci. Lett., 236, 167–181, 2005.

Hirschmann, M. M., A. C. Withers, and C. Aubaud, Petrologic Structure of a Hydrous 410 km Discontinuity, this volume, 2006.

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

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

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

Inoue, T., Y. Tanimoto, T. Irifune, T. Suzuki, H. Fukui, and O. Ohtaka, Thermal expansion of wadsleyite, ringwoodite, hydrous wadsleyite and hydrous ringwoodite, Phys. Earth Planet. Inter., 143–144, 279–290, 2004.

Iwamori, H., Transportation of H2O and melting in subduction zones, *Earth Planet. Sci. Lett., 160,* 65–80, 1998.

Jackson, I., J. D. Fitz Gerald, U. H. Faul, and B. H. Tan, Grain-size-sensitive seismic wave attenuation in polycrystaline olivine, *J Geophys. Res., 107,* doi:10.1029/2001JB001225, 2002.

Jackson, I., M. S. Paterson, and J. D. FitzGerald, Seismic wave dispersion and attenuation in Aheim Dunite: an experimental study, Geophys. J. Int., 108, 517–534, 1992.

Jackson, J. M., J. Zhang, and J. D. Bass, Sound velocities and elasticity of aluminous $MgSiO_3$ perovskite: Implications for aluminum heterogeneity in Earth's lower mantle, Geophys. Res. Lett., 31, L10614, doi: 10.1029/2004GL019918, 2004.

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

Jacobsen, S. D., and J. R. Smyth, Effect of water on the sound velocities of ringwoodite in the transition zone, this volume, 2006.

James, D. E. and I. S. Sacks, Cenozoic formation of the central Andes: A geophysical perspective, Spec. Pub. 7 of the SEG, 1–25, 1999.

James, D. E., M. J. Fouch, J. C. VanDecar, S. van der Lee, and Kaapvaal Seismic Group, Tectospheric structure beneath southern Africa, Geophys. Res. Lett. 28, 2485–2488, 2001.

Jordan, T. H., Structure and formation of the continental tectosphere, J. Petrol. Special Lithospheric Issue, 11–37, 1988.

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

Karato, S., Importance of anelasticity in the interpretation of seismic tomography, *Geophysical Research Letters, 20,* 1623–1626, 1993.

Karato, S.-I., Mapping water content in the upper mantle, in *Inside the Subduction Factory,* edited by J. M. Eiler, pp. 135–152, American Geophysical Union, Washington D.C., 2003.

Karato, S., and H. Jung, Water, partial melting, and the origin of the seismic low velocity zone in the upper mantle, Tectonophysics, 157, 193–207, 1998.

Karato, S., Hydrogen-related defects and their influence on the electrical conductivity and plastic deformation of mantle minerals: a critical review, this volume, 2006a.

Karato, S., Microscopic models for the influence of hydrogen on physical and chemical properties of minerals, in Superplume: Beyond Plate Tectonics, edited by D. A. Yuen, et al., Springer, in press, 2006b.

Kay, S. M., C. Mpodozis, and B. Coira, Magmatism, tectonism, and mineral deposits of the Central Andes (22°–33°S latitude. In Skinner, B. (ed.), Geology and Ore Deposits of the Central Andes, Society of Economic Geology Special Publication (SEG) No. 7, 27–59, 1999.

Kelley, K. A., T. Plank, T. L. Grove, E. M. Stolper, S. Newman, and E. Hauri, Mantle melting as a function of water content at subduction zones I: Back-arc basins, J. Geophys. Res., in press, 2006.

Keppler, H., M. Wiedenbeck, and S.S. Shcheka, Carbon solubility in olivine and the mode of carbon storage in the Earth's mantle, Nature 424, 414–416, 2003.

Kohlstedt, D. L., H. Keppler, and D. C. Rubie, Solubility of water in the α, β, and γ phases of $(Mg, Fe)_2\ SiO_4$, Contrib. Mineral. Petrol., 123, 345–357, 1996.

Komabayashi, T., Phase Relations of Hydrous Peridotite: Implications for Water Circulation in the Earth's Mantle, this volume, 2006.

Lee, C. -T. A., Compositional variation of density and seismic velocities in natural peridotites at STP conditions: implications for seismic imaging of compositional anomalies in the upper mantle, J. Geophys. Res., 108, B9, 2441, doi: 10.1029/2003JB002413, 2003.

Li, L., D. J. Weidner, J. Brodholt, D. Alfe, G.D. Price, R. Caracas, and R. Wentzcovitch, Elasticity of $CaSiO_3$ perovskite at high pressure and high temperature. Phys. Earth Planet. Int., 155, 249–259, 2006.

Lizarralde, D., A. Chave, G. Hirth, and A. Schultz, Northeastern Pacific mantle conductivity profile from long-period magnetotelluric sounding using Hawaii-to-California submarine cable data, *J. Geophys. Res., 100* (B9), 17,837–17,854, 1995.

Mei, S., and D. L. Kohlstedt, Influence of water on plastic deformation of olivine aggregates 1. Diffusion creep regime, *J. Geophys. Res., 105,* 21,457–21,469, 2000a.

Mei, S., and D. L. Kohlstedt, Influence of water on plastic deformation of olivine aggregates 2. Dislocation creep regime, *J. Geophys. Res., 105,* 21,471–21,481, 2000b.

Marone, F., S. van der Lee, and D. Giardini, Three-dimensional upper-mantle S-velocity model for the Eurasia-Africa plate boundary region, Geophys. J. Int., 158, 109–130, 2004.

Matsukage, K. N., Y. Nishihara, and S. Karato, Seismological signature of chemical differentiation of Earth's upper mantle, J. Geophys. Res., 110, doi:/10.1029/2004/JB003504, 2005.

Mavko, G. M., Velocity and attenuation in partially molten rocks, *J. Geophys. Res.*, *85*, 5412–5426, 1980.

Morris, J. D., W. P. Leeman and F. Tera, The subducted component in island arc lavas: constraints from Be isotopes and B-Be systematics, Nature, 344, 31–36, 1990.

Nakajima, J., T. Matsuzawa, A. Hasegawa, and D. Zhao, Three-dimensional structure of Vp, Vs, and Vp/Vs beneath the northeastern Japan arc: implications for arc magmatism and fluids, Journal of Geophysical Research, 106, 21843–21857, 2001.

Neele, F., and R. Snieder, Topography of the 400 km discontinuity from the observations of long period P400P phases, Geophys. J. Int., 109, 670 – 682, 1992.

Nolet, G., and A. Zielhuis, Low S velocities under the Tornquist-Teisseyre zone: evidence for water injection into the transition zone by subduction, J. Geophys. Res., 99, 15813–15820, 1994.

Pearce, J. A., M. Ernewein, S. H. Bloomer, L. M. Parson, B. J. Murton, and L. E. Johnson, Geochemistry of Lau Basin volcanic rocks: influence of ridge segmentation and arc proximity, in Volcanism Associated with Extension at Consuming Plate Margins, *Geol. Soc. Spec. Publ.*, *81*, 53–75, 1995.

Plank, T., and C. H. Langmuir, Tracing trace elements from sediment input to volcanic output at subduction zones, *Nature*, *362*, 739–742, 1993.

Priestley, K., and D. McKenzie, The thermal structure of the lithosphere from shear wave velocities, Earth Planet. Sci. Lett., 244, 285–301, 2006.

Rauch, M. and H. Keppler, Water solubility in orthopyroxene. Contrib. Mineral. Petrol., 143, 525–536, 2002.

Rychert, C.A., K. M. Fischer, and S. Rondenay, A sharp lithosphere-asthenosphere boundary imaged beneath eastern North America, Nature, doi:10.1038/nature03904, 2005.

Revenaugh, J., and S. A. Sipkin, Seismic evidence for silicate melt atop the 410-km mantle discontinuity, Nature, 369, 474–476, 1994.

Rüpke, L., J. Phipps Morgan, and J. Dixon, Implications of Subduction Rehydration for Earth's Deep Water Cycle, this volume, 2006.

Saal, A. E., E. H. Hauri, C. H. Langmuir, M. R. Perfit, Vapour undersaturation in primitive mid-ocean-ridge basalt and the volatile content of Earth's upper mantle, *Nature. 419*, 451–455, 2002.

Schmidt, M. W., and S. Poli, Experimentally based water budgets for dehydrating slabs and consequences for arc magma generation, *Earth Planet Sci Lett*, *163*, 361–379, 1998.

Schutt, D. L., and C. E. Lesher, Effects of melt depletion on the density and seismic velocity of garnet and spinel lherzolite, J. Geophys. Res., 111, 10.1029/2003JB002950, 2006.

Shearer, P., and M. Flanagan, Seismic velocity and density jumps across the 410- and 660-kilometer discontinuities, Science, 285, 1545–548, 1999.

Shito, A., and T. Shibutani, Nature of heterogeneity of the upper mantle beneath the northern Philippine Sea as inferred from attenuation and velocity tomography, *Phys. Earth and Planet. Int.*, *140*, 331–341, 2003.

Shito, A., S. Karato, K. Matsukage, and Y. Nishihara, Toward mapping three-dimensional distribution of water in the upper mantle from combined velocity attenuation tomography: Applications to subduction zone upper mantle, this volume, 2006.

Sinelnikov, Y. D., G. Chen, and R.C. Liebermann, Elasticity of $CaTiO_3$-$CaSiO_3$ perovksites, Phys. Chem. Minerals 25, 515–521, 1998.

Sinogeikin, S.V., J. D. Bass, and T. Katsura, Single-crystal elasticity of gamma -$(Mg_{0.91}Fe_{0.09})_2SiO_4$ to high pressures and to high temperatures, Geophysical Research Letters, 28, 22, 4335–4338, 2001.

Smyth, J. R., and D. J. Frost, The effect of water on the 410-km discontinuity: An experimental study, Geophys. Res. Lett., doi:10.1029/2002GL014418, 2002.

Smyth, J. R., D. J. Frost, and F. Nestola, Hydration of olivine and the Earth's deep water cycle, Geochim. Cosmochim. Acta, 69, A746, 2005.

Smyth, J. R. and S. Jacobsen, Nominally Anhydrous Minerals and Earth's Deep Water Cycle, this volume, 2006.

Song, T. A., and D. V. Helmberger, Low velocity zone atop the transition zone in the western US from S waveform triplication, this volume, 2006.

Suetsugu, D., T. Inoue, A. Yamada, D. Zhao, and M. Obayashi, A study of temperature anomalies and water content in the mantle transition zone beneath subduction zones as inferred from P-wave velocities and mantle discontinuity depths, this volume, 2006.

Taylor, B., and F. Martinez, Back-arc basin basalt systematics, Earth *Planet. Sci. Lett.*, *210*, 481–497, 2003.

Tibi, R. and D. A. Wiens, Detailed structure and sharpness of upper mantle discontinuities in the Tonga subduction zone from regional broadband arrays, J. Geophys. Res., 110, doi:10.1029/2004JB003433, 2005.

Takei, Y., Effect of pore geometry on Vp/Vs: From equilibrium geometry to crack, *J. Geophys. Res.*, *107*, 10.0129/2001JB000522, 2002.

Tatsumi, Y., and S. Eggins, *Subduction Zone Magmatism*, 211 pp., Blackwell, Cambridge, MA, 1995.

Trampert, J., F. Deschamps, J. Resovsky, and D. Yuen, Probabilistic Tomography Maps Chemical Heterogeneities Throughout the Lower Mantle, Science, 306, 853–856, 2004.

Vidale, J. E., X. Y. Ding, and S.P. Grand, The 410-km-depth discontinuity: A sharpness estimate from near-critical reflections, Geophys. Res. Lett., 22, 2557–2560, 1995.

Van der Lee, S. and G. Nolet, Upper-mantle S-velocity structure of North America, J. Geophys. Res., 102, 22,815–22,838, 1997.

Van der Lee, S., D. James and P. Silver, Upper-mantle S-velocity structure of western and central South America, *J. Geophys. Res.*, 106, 30821–30834, 2001.

Van der Lee, S., D. James and P. Silver, Correction to "Upper-mantle S-velocity structure of western and central South America", by Suzan van der Lee, David James, and Paul Silver, J. Geophys. Res., 107, DOI 10.1029/2002JB001891, 2002.

Van der Lee, S., F. Marone, M. van der Meijde, D. Giardini, A. Deschamps, L. Margheriti, P. Burkett, S. C. Soloman, P. M.

Alves, M. Chouliaras, A. Eshwehdi, A. Suleiman, H. Gashut, M. Herak, R. Ortiz, J. M. Davila, A. Ugalde, J. Vila, and K. Yelles, Eurasia-Africa plate boundary region yields new seismographic data, Eos Trans. AGU, 82, 637–646, 2001.

Van der Lee, S. and A. Frederiksen, Surface wave tomography applied to the North America upper mantle, in Seismic Earth: Array *Analysis of Broadband Seismograms*, edited by A. Levander and G. Nolet, American Geophysical Union, GM 157, 67–80, 2005.

Van der Lee, S., K. Regenauer-Lieb, and D. Yuen, The role of water in connecting past and future episodes of subduction, submitted manuscript, 2006.

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

Wiens, D. A., N. Seama, and J. A. Conder, Mantle structure and flow patterns beneath active backarc basins inferred from passive seismic and electromagnetic methods, in *Interactions among physical, chemical, biological, and geological processes in back-arc spreading systems*, edited by D. Christie, p. in press, American Geophysical Union, Washington D.C., 2006a.

Wiens, D. A., K. Kelley, and T. Plank, Mantle Temperature Variations Beneath Back-arc Spreading Centers Inferred from Seismology, Petrology, and Bathymetry, Earth and Planetary Science Letters, in press, 2006b.

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

Yamazaki, A., and K. Hirahara, The thickness of upper-mantle discontinuities, as inferred from short-period J-Array data, Geophys. Res. Lett., 21, 1811–1814, 1994.

Yuan, X., S. V. Sobolev, R. kind, O. oncken, G. bock, G. Asch, B. Schurr, F. Graeber, A. Rietbrock, P. Giese, P. Wigger, P. Rower, G. Zandt, S. Beck, T. Wallace, M. Pardo, and D. Comte, Subduction and collision processes in the Central Andes constrained by converted seismic phases, *Nature*, *408*, 958–561, 2000.

Zhao, D., Global tomographic images of mantle plumes and subducting slabs: insight into deep Earth dynamics, Phys. Earth Planet. Inter., 146, 3–34, 2004.

Zhao, D., D. Christensen, and H. Pulpan, Tomographic imaging of the Alaska subduction zone, *J. Geophys. Res*, *100*, 6487–6504, 1995.

Zhao, D., A. Hasegawa, and S. Horiuchi, Tomographic imaging of P and S wave velocity structure beneath Northeastern Japan, *J. Geophys. Res.*, *97*, 19,909–19928, 1992.

Zhao, D., Y. Xu, D. A. Wiens, L. Dorman, J. Hildebrand, and S. Webb, Depth extent of the Lau back-arc spreading center and its relationship to the subduction process, *Science*, *278*, 254–257, 1997.