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HYDROGEN IN THE DEEP EARTH

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■ **Abstract** The mechanisms of exchange of hydrogen between the deep interior and surface of Earth, as well as the means of retention and possible abundance of hydrogen deep within the Earth, are examined. The uppermost several hundred kilometers of Earth's suboceanic upper mantle appear to be largely degassed, but significant primordial hydrogen could be retained within the transition zone, lower mantle, or core. Regassing of the planet occurs via subduction: Cold slabs are likely particularly efficient at transporting hydrogen to depth within the planet. Marked changes in hydrogen cycling have taken place throughout Earth's history: Evidence of hydrated ultramafic melts in the Archean and probable hydrogen retention within a Hadean magma ocean indicate that early in its history, the deep Earth was substantially wetter. The largest enigma associated with hydrogen in the deep Earth lies in the core: This region could represent the dominant reservoir of hydrogen on the planet, with up to ∼100 hydrospheres of hydrogen present as a high-pressure iron-alloy.

INTRODUCTION

Hydrogen is the most abundant element in the solar system, and together with oxygen, which ranks third, it forms water—ubiquitous at the Earth's surface and, in liquid form, arguably the distinguishing feature of this planet. Despite its cosmic ubiquity, the elemental abundance of hydrogen within our planet has been enigmatic. Estimates of the hydrogen abundance in Earth's interior have spanned a range from less than the equivalent of the current hydrosphere to on the order of 100 hydrospheres if hydrogen is the dominant light alloying component in Earth's outer core. The underlying unanswered question here, pivotal for our understanding of Earth's evolution, is how efficiently is our planet's interior degassed.

The uncertainties about the abundance of hydrogen in the planet are striking, given both the profound effect of hydrogen on properties and processes on microscopic-to-global scales, and its primary roles in the evolution of the planet. These effects include its demonstrable weakening of rocks and minerals and the

major effects it has on phase relations, especially the dramatic depression of the solidus, and on the formation of hydrous high-pressure phases. The geologic manifestations of the presence of water and its interactions with the interior have produced the major distinguishing topographic features of our planet, including continents [generated by hydrous melting (Campbell & Taylor 1983)] and probably the narrow zones at mid-ocean ridge crests at which new plate is produced [generated by dehydration-induced strengthening of the oceanic upper mantle during partial melting (Hirth & Kohlstedt 1996)]. At higher pressures, uncertainties about the amount of hydrogen in mantle and core materials give rise to variations of a thousand degrees in the inferred temperature profile of Earth's core. Moreover, it has long been inferred that the source of the hydrosphere was degassing from Earth's solid mantle (e.g. Rubey 1951). Thus, the behavior and abundance of hydrogen in the planet is key to understanding the evolution, dynamic state, and thermal structure of not only the deep interior, but ultimately the evolution of the crust and hydrosphere as well.

Recent work across a broad range of disciplines has resulted in new views about hydrogen in the Earth. Materials studies have established that the extreme pressure-temperature conditions characteristic of the deep interior impart dramatic changes in bonding properties associated with hydrogen, precluding extrapolation of the behavior of materials studied under near-surface conditions. Mineralogical studies of the past several decades have established that nominally anhydrous phases can contain significant amounts of hydrogen as defects (e.g. Bell & Rossman 1992, Ingrin & Skogby 2000). If the amount of hydrogen found in these phases is representative of the entire mantle, then a volume of water at least as large as the current oceans could be retained within Earth's silicate mantle without the presence of separate hydrous phases at depth. Moreover, new classes of dense hydrous phases have been discovered (Prewitt & Parise 2000). Furthermore, recent experiments provide possible new constraints on the abundance of hydrogen (along with other light elements) in the core (e.g. Jana & Walker 1999).

In tandem with these experimental advances, the role of water in generating voluminous mantle melting has been recently reexamined, with water having been proposed as playing a principal role in the genesis of continental flood basalts and the genesis of komatiites, a major ultramafic rock type of the Archean (Turner & Hawkesworth 1995, Parman et al 1997). Additionally, enhanced attention has been directed to the manner in which water was incorporated within the earliest Earth, from its meteoritic and cometary origins to its likely incorporation and retention within a primordial magma ocean (e.g. Lecuyer et al 1998, Righter & Drake 1999). A backdrop to these terrestrial issues is the evidence of significant water abundances elsewhere in the solar system, including polar caps and channels on Mars as well as the recent observational evidence of large subsurface quantities of water on Mars (Malin & Edgett 2000, Zuber et al 2000). Suggestions have been made that large quantities of hydrous phases could be present on Europa, as well (McCord et al 1999).

This article attempts to systematically review many of these interrelated questions. We are not concerned with hydrogen cycling and exchange in the near-surface

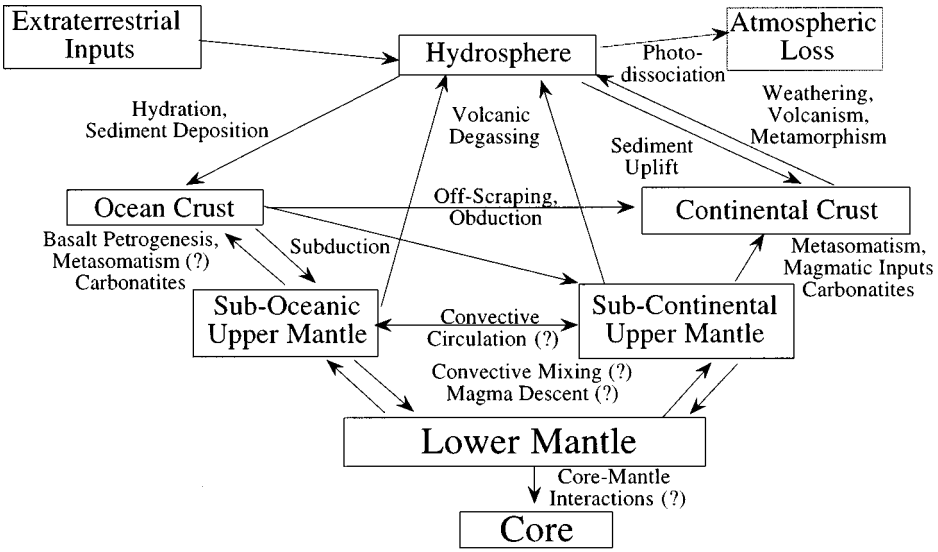

Figure 1 Box diagram of different reservoirs for water on Earth. Labeled arrows show likely directions and processes of hydrogen exchange between different reservoirs.

environment (which we loosely define as extending to normal crustal depths), as this has been the subject of numerous previous reviews. Instead, we focus on constraints on volatile retention and cycling in the lower four hydrogen reservoirs shown in Figure 1. Yet we recognize that the characteristics of hydrogen in the shallower reservoirs (Figure 1) provide crucial observational baselines and ground truths for any discussion of the fate of hydrogen at depth. These include forms as diverse as the deuterium/hydrogen (D/H) ratio of the hydrosphere or the degree of hydration of deep-seated magmas and xenoliths that have been emplaced at the surface. The review is organized as follows. We first examine evidence related to hydrogen recycling between the hydrosphere and the deep Earth. We then review the mineralogic mechanisms by which hydrogen can be transported to, and retained within, the deep Earth. We conclude with a discussion of the likely history of hydrogen incorporation, retention, and cycling in the deep Earth.

OBSERVATIONAL CONSTRAINTS ON HYDROGEN DEGASSING AND REGASSING FROM THE MANTLE

Subduction-Related Regassing

Plate tectonic processes represent the dominant means at present for exchange of water between the interior and the hydrosphere. Indeed, the subduction of oceanic lithosphere into the underlying mantle appears to lead to reincorporation of water in the mantle. This is because the amount of degassing observed in arc-magmatic

systems is, with broad uncertainties, approximately an order of magnitude less than the amount that is subducted (e.g. Gill 1981, Ito et al 1983, Peacock 1990, Bebout 1995). The uncertainties in this comparison are multifold. First, the amount of pelagic sediment that is actually subducted beyond the accretionary prism is ill constrained [although it is clear from observations of the cosmogenic nuclide ^{10}Be in arc magmas that some sediments must be carried to a depth of at least 100–150 km, the actual amount subducted is generally assumed to be a default value, such as a 200-m column of sediments (Peacock 1990)]. Second, the degree (and depth dependence) of hydration/hydrothermal alteration of the oceanic crust is unknown. Third, the amount of water that is actually transported to depth relative to that emplaced within the overlying plate/mantle wedge or returned to the surface along the decollement between the two plates (e.g. Moore & Vrolijk 1992) is unknown. That is, the role of igneous intrusions and subduction-associated metamorphism in retaining or diffusely degassing water within the arc at depth is ill constrained, as is the absolute volume of water that escapes along the interplate shear zone.

In spite of these broad uncertainties, the estimated magnitudes of the flux of water into subduction zones and their corresponding degassing rates provide a first-order indication that subduction zones act as major sinks of water: Peacock (1990) infers that 8.7×10^{11} kg of H_2O/year is subducted, with 1.4×10^{11} kg/year being returned through arc magmatism. Thus, if current rates of volatile subduction and return provide a representative estimate for these rates in post-Archean Earth, we would infer that 7.3×10^{20} kg of water would be subducted every billion years. This corresponds to approximately half the size of the current hydrosphere being transported to depth via subduction every billion years. The interest of this number is simply that the hydration of sediments and the oceanic crust is produced directly from interactions with seawater, and the subduction process thus provides a direct linkage between the hydrosphere and deep Earth.

How much water ultimately reaches the deep Earth in the subduction process is likely governed by the stability of high-pressure hydrous metamorphic phases, such as lawsonite, as described below. From the point of view of the geochemical evolution of the mantle, the role of subduction in the cycling of water is likely twofold: First, subduction plausibly enriches both the mantle wedge and lithospheric mantle and the deep crustal portions of the overriding plate in volatile components; and second, prior to either the dehydration or ultimate homogenization of the hydrated portions of subducted slabs through convective stirring and diffusive processes, subduction introduces localized, water-enriched zones into the deep Earth. That portions of the continental lithospheric mantle are water enriched is well documented: Not only are deeply exhumed, ultramafic complexes observed to contain hydrous phases that formed at high pressures (Scambelluri et al 1995), but mantle-derived mica- and amphibole-bearing xenoliths are observed in a range of continental volcanic environments (e.g. Dawson & Smith 1977, Boettcher & O'Neil 1980, Dyar et al 1993, Agrinier et al 1993). These observations of hydration of lithospheric mantle are in accord with calculations of the thermal structure and phase equilibria of hydrous phases in these environments (Peacock 1993, Wyllie

1978). Observations of water-rich fluid inclusions in diamonds indicate that deeper subcontinental (and likely sublithospheric) mantle has been exposed to hydrous metasomatic fluids (Schrauder & Navon 1994). This subcontinental water enrichment may be profoundly important for planetary magmatism, with small quantities of water (~0.4%) having been proposed as playing a pivotal role in the generation of voluminous continental flood basalts (Gallagher & Hawkesworth 1992, Turner & Hawkesworth 1995). This possible linkage between water and flood basalt generation indicates the effect that even comparatively small degrees of hydration of Earth materials can have in producing phenomena of considerable geodynamic and petrologic importance.

Degassing of the Mantle

The production of basalt at mid-ocean ridges and hot spots is generally regarded as a primary mechanism by which water is extracted from the mantle: how much of this water is simply retained within the oceanic crust until it is subducted, and how much enters into the hydrosphere is unclear (e.g. Ito et al 1983). The water content of basalts does, however, provide prima facie constraints on the abundance and nature of water held within the shallow mantle. Indeed, since the pioneering study of Moore (1970), such studies of basalts have been used to place limits on the possible abundance of water in the suboceanic mantle (Michael 1988, Byers et al 1986, Delaney et al 1978, Dixon et al 1988, Sobolev & Chaussidon 1996). Although wide variations in water content are common (Delaney et al 1978), near-primary basaltic compositions (those that have not experienced significant fractional crystallization) have water contents that range from ~700 to ~6000 ppm. For comparison, characteristic amounts of water in basalts from back-arc basins lie between 1.0 and 2.9 wt% (Sobolev & Chaussidon 1996), which demonstrates the importance of water in generating the geochemical characteristics of subduction-related basalts (Stolper & Newman 1994).

The amount of water enrichment in mid-ocean ridge basalts (MORB) commonly correlates with the enrichment in elements that are incompatible in the solid mineral phases from which MORB is derived, such as K, Nb, Ce, and Nd (e.g. Michael 1988, Dixon et al 1988, Sobolev & Chaussidon 1996, Danyushevsky et al 2000). These results demonstrate that water behaves as a component that partitions into the magma with a bulk partition coefficient near 0.01. Such a partition coefficient indicates that water is more compatible than K in MORB and generally comparable in geochemical behavior to rare-earth elements such as Ce, La, and Nd. When these measurements of the water contents of basaltic magma are coupled with the estimated partitioning behavior of water and probable degree of melting associated with MORB, the likely water content of the source material can be estimated. As such, these abundances allow a first-order constraint on the abundance of water and its degree of heterogeneity in the upwelling subridge mantle.

For mantle sources that are depleted in incompatible elements [normal MORB (N-MORB)], a mantle water content of the order of 80–180 ppm is inferred;

for those that are more enriched in such elements (E-MORB), estimated source region abundances are between 200 and 950 ppm (Michael 1988, Sobolev & Chaussidon 1996). Three primary questions emerge from such data: (*a*) How is this water sequestered in the mantle; (*b*) because these abundances reflect average source compositions, how homogeneously distributed is this sequestered water; and (*c*) how representative of the upper mantle is this sampling or how much of the mantle does the mid-ocean ridge system sample? The first of these questions has been probed from a petrologic and mineralogic viewpoint, whereas the latter two questions are at least partially geodynamic in character.

The degree of heterogeneity of the MORB source region is critical for assessing how water may be contained in this zone. Whether MORB is generated from a largely homogeneous source region or from depleted mantle interspersed with geochemically enriched pockets or veins is a topic of longstanding discussion. Recently, trace and major elemental and isotopic evidence has indicated that the geochemistry of MORB is produced by a mixing of melts derived from enriched and depleted components. The enriched component is likely associated with garnet pyroxenite (and possibly meta-basalt) inclusions in the mostly depleted peridotite MORB source region (Lundstrom et al 1995, Hirschmann & Stolper 1996, Bourdon et al 1996). This concept is a straightforward manifestation of the "marble-cake" mantle hypothesis, originally proposed based upon the presence of pyroxenite veining in peridotite massifs (Allegre & Turcotte 1986). Indeed, if a portion of the enriched component of MORB represents fossil oceanic crust recycled into the MORB source region (e.g. Hanan & Graham 1996), then the presence of water within MORB represents the final cycling of subducted water.

The possible presence of geochemically enriched components in the MORB source region is critically important for the means of retention of water in minerals: If this region were largely chemically homogeneous, then the water content of the N-MORB source is such that nominally anhydrous phases could retain most, if not all, of the average concentration of 80–180 ppm of water present in this zone (Bell & Rossman 1992, Dobson et al 1995, Ingrin & Skogby 2000). However, if most of the water in the MORB source region resides in geochemically enriched pods, then water contents in these enriched regions could be over an order of magnitude higher than the inferred average of this region, based upon the likely abundance of enriched garnet pyroxenite veins in the N-MORB source region (Hirschmann & Stolper 1996). These higher water contents would probably require the presence of a separate hydrous phase in the MORB source region. Moreover, the higher water contents of E-MORB and MORBs that are intermediate between E-MORB and N-MORB (occasionally referred to as transitional or T-MORB) may simply reflect a greater abundance of enriched zones within the source region rather than an enhancement of the bulk water content of the entire source region. The pivotal uncertainty in such an analysis lies in the actual composition(s) of the component in the MORB source that gives rise to the enriched signatures.

The idea that amphibole (of uncertain chemistry) and/or phlogopite are primary upper mantle hydrous phases is generally compatible with the frequently observed

correlation between K and water content in MORB (e.g. Michael 1988). Although amphibole is likely to be stable in nonupwelling regions of the mantle, the thermal regime beneath mid-ocean ridges as well as continued interaction with liquid at depths shallower than 70–100 km makes the presence of any amphibole unlikely once large-scale melting has been initiated (Thompson 1992). Phlogopite has been reported to have a relatively large thermal stability field at modest pressures, with a reported maximum temperature of existence of between 1180° and 1300°C near 4 GPa in peridotite assemblages (Kushiro et al 1967, Olafsson & Eggler 1983). In spite of the possible stability of phlogopite, the observation that mantle potassium contents are generally low limits its possible abundance, and thus its water-carrying capacity. This limitation has led to the proposal that an additional, non–K-rich and reasonably refractory hydrous phase may be present within the MORB source region at depths greater than about 70 km (Michael 1988). Within a few MORB samples, an observed decoupling of water and potassium contents indicates that the source for the water need not be associated with a potassium-bearing phase, such as amphibole or phlogopite: This K-poor water source has been proposed to be an H_2O-bearing, CO_2-rich fluid (Sobolev & Chaussidon 1996). Accordingly, it appears that two different origins may exist for the observed water within MORB: Some water could have been produced through dehydration of a K-bearing hydrous phase, whereas some MORB samples require an additional water-bearing phase within their source region. This additional phase may be associated with high-pressure hydrous phases or hydration of nominally anhydrous phases, or it may indicate the presence of a (possibly CO_2 rich) mantle fluid associated with the petrogenesis of MORB. Regardless of the precise identity of this inferred hydrated phase, the available data on MORB indicate that water transport from depth within the mantle occurs beneath ridges, and that an upward flux of water thus occurs in this region.

In contrast to the water contents of erupted MORB, data are comparatively limited on the water contents of primary melts from ocean-islands/hot spots. The water contents of glasses from the mid-Atlantic ridge in close proximity to the Azores and Iceland hot spots are enriched by factors of 2–4 relative to the surrounding mantle (Schilling et al 1983, Kingsley & Schilling 1995). This enhancement is in accord with the general tendency of geochemically enriched sources to be more water enriched and has even led the Azores and Iceland to be referred to as mantle "wetspots" (Schilling et al 1983). If the melting regime associated with hot spots samples more deeply than MORB, then the higher water content of these hot spots could indicate a net increase in the amount of retained water at depth within the planet. Again, as with the observed chemistry of MORB, the known properties of hot spot–associated magmas provide indications of moderate quantities of deep-seated water retained within the deep upper mantle. Other magmatic types also may provide indications of the presence of deep-seated water in Earth's mantle. In a study of the H_2O-saturated solidus of a model mantle composition, Kawamoto & Holloway (1997) found that experimental partial melts near 10 GPa are close in chemistry to kimberlitic magmas. This suggests that kimberlites could be derived

from relatively low-temperature melting of an H_2O-rich mantle at depths of 150–300 km, and it implies that the major diamond-producing deposits of the planet could be associated with hydrous melting processes.

A key question is the extent to which substantial amounts of water are reintroduced into the mantle through subduction processes relative to the amount of water retained within the mantle from the Earth's accretion (Ahrens 1989). Outside of such regions as back-arc basins that are obviously dominated by subducted water, the history of mantle water remains a difficult issue to resolve. As discussed below, D/H ratios do not provide diagnostic constraints on whether water degassed from the mantle has been cycled through the surface hydrosphere and subducted. Yet, based on the water content of erupted basalts, three key observations can be made concerning the distribution of water in Earth's mantle. First, the MORB source region appears grossly globally homogeneous with respect to its average water content [with modest regional variations (Michael 1995)], implying that either subducted water has been remixed relatively homogeneously into the MORB source region, or that the MORB source region has undergone reasonably uniform degassing throughout Earth's history. Yet this observation of gross global homogeneity does not preclude local, lithologically controlled variations in water content. Second, zones associated with deep mantle upwellings (such as hot spots) have been associated with regions of higher water content than the normal MORB source region. Third, abundant evidence from xenoliths (and possibly from continental flood basalts) indicates that at least portions of the subcontinental upper mantle are significantly hydrated. Two end-member possibilities thus exist: (*a*) The bulk of primordial water in the mantle has been degassed, and subduction over the course of Earth's history has rehydrated the oceanic upper mantle at a low level, with deeper depth levels prospectively retaining modestly more subducted water; or (*b*) subducted water has been dominantly emplaced either shallowly in the subcontinental upper mantle, or below the MORB source region (perhaps within the lower mantle), with relatively little recycling into the oceanic upper mantle. In the latter scenario, the bulk of Earth's oceanic upper mantle would retain primordial water at the 100-ppm level, with the amount of primordial hydration (and prospectively subduction-induced hydration) increasing with depth. The key issues here are not only the ultimate fate of subducted material and the efficiency with which the planet has degassed, but also the degree of exchange of water between different mantle reservoirs (Figure 1).

HYDROGEN IN THE DEEP MANTLE

Structure and Bonding of Hydrogen

Any discussion of the fate and role of hydrogen-bearing material at depth must consider the fundamental properties of structure and bonding (e.g. speciation) in solid and fluid phases that form (or have formed) at depth within the planet. In materials of the near-surface environment (e.g. crustal minerals and fluids), hydrogen is

commonly incorporated as OH^- and H_2O, with "free" protons usually considered bound as H_3O^+, $H_5O_2^+$, and NH_4^+ (Hawthorne 1992, Prewitt & Parise 2000). As noted below, the incorporation of hydrogen as hydroxyl can form relatively dense structures that are directly related to equivalent anhydrous structures by simple substitution and/or crystallographic shearing mechanisms (Finger & Prewitt 1989, Prewitt & Parise 2000). Another mechanism is the so-called hydrogarnet substitution, the exchange of $4H^+$ for Si^{4+} (or $3H^+$ for Al^{3+}) (Lager et al 1989, Wright et al 1994, Armbruster 1995, Lager & VonDreele 1996; for a more detailed discussion, see Prewitt & Parise 2000). In addition, hydrogen in core-forming metal alloys can be considered a hydride (H^-) (Fukai 1993).

A central concept is the hydrogen bond and its response to the range of pressures, temperatures, and chemical composition found within the Earth. Conventionally, the hydrogen bond is considered to occur in a linear O-H¨O unit and involves the pairing of a weak O¨H and strong (covalent) O-H linkage. The strength of hydrogen bonding in such a linkage depends on the oxygen-oxygen distance and O-H¨O bond angle. Extensive work has been conducted on simple hydroxides such as $Mg(OH)_2$ and $Ca(OH)_2$ under pressure to provide a systematic basis for evaluating the effect of pressure on the hydrogen bond (Kruger et al 1989, Duffy et al 1991, Fei & Mao 1993, Johnson & Walker 1993, Parise et al 1994, Catti et al 1995, Nagai et al 2000). Yet, a range of spectroscopic and crystallographic studies have shown that hydrogen bonding can either increase or decrease on compression, depending on crystal structure and composition (Williams 1992, Cynn & Hofmeister 1994, Faust & Williams 1996, Williams & Guenther 1996, Liu et al 1997a,b, Liu et al 1998a,b, Hemley et al 1998, Lu et al 1999, Hofmeister et al 1999, Scott & Williams 1999, Kagi et al 2000). High-pressure polymorphism in hydrous phases is likely to be strongly influenced by pressure-induced variations in hydrogen bonding (Faust & Williams 1996). Neighboring cations and pressure-induced changes in the bonding properties of the oxygen anion may each also play a role in the magnitude of hydrogen bonding at pressure (Williams & Guenther 1996, Larsen & Williams 1998). Moreover, at the very highest pressures, the conventional (ambient pressure) concept of the hydrogen bond is no longer valid in such materials, where a symmetric hydrogen bonded state can exist. The prototypical case is the symmetric hydrogen-bonded phase of H_2O at 60 GPa (Aoki et al 1996, Goncharov et al 1996). Compression of the O-H¨O group in this system gives symmetric hydrogen bonding with distances of 2.38–2.40 Å.

These changes in bonding properties induced by pressure (and temperature) may have significant effects on physical properties, as detailed below. The weakened covalent OH bonds under pressure may give rise to large anharmonic effects prior to melting, including weakening of materials and possible diffusive behavior or superionic conductivity (e.g. as predicted for subsolidus H_2O) (Cavazzoni et al 1999). Such behavior would stabilize the solid to higher temperature as well as provide a possible mechanism for attenuation at seismic frequencies (i.e. even in the absence of the production of a free H_2O-rich fluid phase). A related phenomenon occurs on metastable compression of some hydrous materials: Pressure alone can

induce a disordering of the hydrogen sublattice (Duffy et al 1995a,b; Nguyen et al 1997; Parise et al 1998), perhaps driven by increased hydrogen-hydrogen repulsion on compression. In some materials, the disordering can be viewed as amorphization. Such low-temperature metastable transitions have been proposed as the origin for large-scale phenomena such as deep-focus earthquakes (i.e. driven by pressure-induced amorphization/dehydration in serpentine) (Meade & Jeanloz 1991), but this is not supported by high-pressure experiments carried out at higher (and thus relevant) temperatures (Irifune et al 1996, Kuroda & Irifune 1998).

Hydrogen in Nominally Anhydrous Mantle Phases

Upper Mantle Phases The possibility that nominally anhydrous mantle phases could take up significant quantities of water as crystallographic defects has long been considered (e.g. Fyfe 1970). Garnets provided the prototype for such a substitution, as a complete solid solution exists at low pressures between $Ca_3Al_2Si_3O_{12}$-grossular and $Ca_3A_2(O_4H_4)_3$-hydrogarnet. Both the manner in which O_4H_4 groupings substitute for SiO_4 tetrahedra and the effect of this substitution on the physical properties of garnet have been extensively probed (e.g. Lager et al 1989, Knittle et al 1992, O'Neill et al 1993). Yet the maximum amount of water that can be taken up through the O_4H_4 substitution by the magnesium-rich garnets present in Earth's mantle is much smaller than those of calcium-rich garnets: on the order of 500 ppm, or 0.05 wt% (Ackermann et al 1983, Lu & Keppler 1997). This amount is about an order of magnitude larger than typical amounts of water present in garnets in mantle xenoliths (Aines & Rossman 1984, Bell & Rossman 1992), and there are indications that the manner in which some of the water substitutes into natural garnets may be more complex than the hydrogarnet substitution (Lager et al 1989, Lu & Keppler 1997).

Indeed, xenolithic samples of each of the other major upper mantle phases, olivine, orthopyroxene, and clinopyroxene, contain variable amounts of structurally bound water as defects. The orthopyroxenes typically contain between 200 and 650 ppm of water, whereas mantle-derived olivines generally have below 100 ppm of water (Miller et al 1987, Skogby et al 1990, Bell & Rossman 1992, Kohn 1996, Keppler & Rauch 2000, Ingrin & Skogby 2000), although somewhat larger contents have been reported (Kurosawa et al 1992). In olivine, some of these defects involve planar layers that resemble intercalations of lamellae several angstroms thick of clinohumite or chondrodite-type structures (Kitamura et al 1987) (see Table 1). Aside from the few observations of such planar features, the detailed crystal chemistry of these defects remains uncertain, but they likely involve the substitution of OH-hydroxyl units for oxygen ions coupled with the formation of Mg^{2+} or Si^{4+} vacancies to charge balance (e.g. Libowitzky & Beran 1995). Some defects may also be associated with interstitial oxygen ions (Bai & Kohlstedt 1993). Regardless of the precise structural origin of these defects, the diffusion rate of hydrogen in olivine indicates that dissolved water would be lost on a timescale of hours on ascent from depth at temperatures in excess of 800°C

(Mackwell & Kohlstedt 1990). Although few data are available on hydrogen diffusion rates in other mantle phases, it is probable that the estimates of water contents on minerals in mantle-derived xenoliths probably represent lower estimates of the amount of water present at depth.

The experimental situation with respect to defect water solubility in olivine has been examined in moderate detail (Bai & Kohlstedt 1993, Young et al 1993, Kohlstedt et al 1996). The solubility of water in olivine increases rapidly with pressure, ultimately reaching a maximum value of near 0.12 wt% (1200 ppm) at temperatures of 1100°C at pressures corresponding to those present at a depth of 400 km (Kohlstedt et al 1996). If this solubility is used as an upper bound for that present throughout the upper mantle, then the amount of water that could be retained in nominally anhydrous olivine alone within the upper mantle is limited to an absolute maximum of 10%–15% of the present mass of the hydrosphere (and more probably lies in the 0.5%–1.5% range). This comparatively small amount indicates that defect substitution of water into nominally anhydrous phases is unlikely to drastically alter the estimated bulk water content of the planet: Rather, the primary importance of such defect water lies principally in its effects on electrical and viscous transport properties, and on the chemistry of low-degree partial melts. These effects are discussed in more detail below.

Notably, the amount of water observed within "anhydrous" phases in mantle xenoliths (of the order of 100 ppm) is in gross accord with the average amount of water inferred to be present in the source region of N-MORB, but below the average content of 200–950 ppm inferred for the source region of E-MORB (e.g. Michael 1988, Sobolev & Chaussidon 1996). As such, the concentrations of water in the E-MORB source region may exceed the amount able to enter into nominally anhydrous phases (particularly if the water is heterogeneously distributed), thus possibly requiring the presence of a separate hydrous phase.

Defect Substitution in Transition Zone Phases Considerable recent attention has been focused on defect substitution of hydrogen into the phases of the transition zone. In particular, efforts have been made to establish the effect of water on the phase relations among the polymorphs (α, β, and γ phases) of $(Mg,Fe)_2SiO_4$. Systematic studies of phase relations as a function of pressure and temperature have demonstrated that the stability field of the high-pressure β-phase expands into both the α-olivine and γ-spinel fields when H_2O is present (e.g. Gasparik 1993, Lu et al 1996). Indeed, in apparent contrast to the limited solubility of water in olivine, the high-pressure β-phase (which likely dominates Earth's mantle between a depth of 400 and 520 km) has been observed to take up quantities of water as high as 3.1 wt% (e.g. McMillan et al 1991, Young et al 1993, Gasparik 1993, Cynn & Hofmeister 1994, Inoue 1994, Inoue et al 1995), confirming predictions by Smyth (1987, 1994). The crystal-chemical underpinnings of this defect substitution are straightforward: β-$(Mg,Fe)_2SiO_4$ contains Si_2O_7 units, unlike the isolated SiO_4-tetrahedra present in olivine and γ-spinel. Therefore, 0.5 oxygens per formula unit in β-phase are not bound to a silicate tetrahedra but are

TABLE 1 Selected hydrous phases of Earth's mantle[a]

Mineral name	Formula[b]	Density[c]	H Content (wt%)[d]	Stability[e]	References
Phase A	$Mg_7{}^{IV}Si_2O_8(OH)_6$	2.96	1.3%	6–10 GPa, ~1000°C	Ringwood & Major 1967, Wunder 1998
Phase B	$Mg_{24}{}^{IV}Si_2{}^{VI}Si_6O_{38}(OH)_4$	3.32–3.38	0.3	12–24 GPa, ~1000°C	Ringwood & Major 1967, Finger et al 1989
Superhydrous B	$Mg_{10}{}^{IV}Si_2{}^{VI}SiO_{14}(OH)_4$	3.21–3.33	0.7	12–24 GPa, 1300°C	Gasparik 1989, Pacalo & Parise 1992
Phase E[f]	$Mg_{2.3}{}^{[IV+VI]}Si_{1.25}H_{2.4}O_6$	2.78–2.92	1.3	12–15 GPa, 1100°C	Kanzaki 1989, Inoue 1994, Shieh et al 2000b
Phase D	$Mg^{VI}Si_{2-x}H_{2+4x}O_6$[g]	3.50	1.1	4–~50 GPa, ~2400°C	Liu 1987, Irifune et al 1998, Shieh et al 1998
10-Å Phase	$Mg_3{}^{IV}Si_4O_{10}(OH)_2H_2O$	~2.65	1.0	3–9 GPa, 500°C	Sclar et al 1965, Yamamoto & Akimoto 1977
Brucite	$Mg(OH)_2$	2.37	3.4	>78 GPa,[h] 1300°C	Duffy et al 1991, Fei & Mao 1993, Johnson & Walker 1993
Serpentine[i]	$Mg_3{}^{IV}Si_2O_5(OH)_4$	2.55	1.5	5 GPa, 700°C	Ulmer & Tromsdorff 1995, Wunder & Schreyer 1997
Norbergite[j]	$Mg_3{}^{IV}SiO_4(OH)_2$	3.19	1.1	>5 GPa, 1100°C	Yamamoto & Akimoto 1977, Papike 1987
Chondrodite	$Mg_5{}^{IV}Si_2O_8(OH)_2$	3.06–3.16	0.6	10 GPa, 1100°C	Akimoto & Akaogi 1980, Wunder 1998
Humite	$Mg_7{}^{IV}Si_3O_{12}(OH)_2$	3.10	0.6	>3 GPa, 900°C	Liu 1993, Wunder et al 1995
Clinohumite[k]	$Mg_9{}^{IV}Si_4O_{16}(OH)_2$	3.14–3.26	0.3	>10 GPa, >1000°C	Yamamoto & Akimoto 1977, Kanzaki 1991, Wunder 1998
Lawsonite	$CaAl_2({}^{IV}Si_2O_7)(OH)_2H_2O$	3.09	1.3	2–11 GPa, ~800°C	Pawley 1994, Schmidt 1995

Phlogopite	$K_2(Mg,Fe^{2+})_6{}^{IV}Si_6Al_2O_{20}(H,F)_2$	2.78	0.3	>10 GPa, ~1000°C	Sudo & Tatsumi 1990, Liu 1993
K-Richterite	$K_2Ca(Mg,Fe^{2+})_5{}^{IV}Si_8O_{22}(OH)_2$	3.01	0.2	5 GPa, 1200°C	Inoue et al 1998
Phase X	$K_4Mg_8{}^{IV}Si_8O_{25}(OH)_2$ (?)	2.95–3.28	(0.3)	17 GPa, 1600°C	Luth 1997, Inoue et al 1998
Zoisite	$Ca_2Al_3{}^{IV}Si_3O_{12}(OH)$	3.15	0.2	4 GPa, 700°C	Poli & Schmidt 1998
Talc	$Mg_3{}^{IV}Si_4O_{10}(OH)_2$	2.78	0.5	5 GPa, 700°C	Yamamoto & Akimoto 1977
Topaz-OH	$Al_2{}^{IV}SiO_4(OH)_2$	3.37	1.1	11 GPa, 1000°C	Wunder et al 1993a,b
Diaspore	AlOOH	2.38	1.7	6 GPa, 400°C	Wunder et al 1993a,b
Phase “pi”	$Al_3{}^{IV}Si_2O_7(OH)_3$	3.23	1.0	6 GPa, 700°C	Wunder et al 1993a,b
Phase “egg”	$Al^{VI}SiO_3OH$	3.84	0.8	>11 GPa, 1300°C	Schmidt et al 1998
Mg-pumpellyite	$Mg_5Al_5{}^{IV}Si_6O_{21}(OH)_7$	~3.3	0.8	~6 GPa, 770°C	Artioli et al 1999
Wadsleyite I	$Mg_7{}^{IV}Si_4O_{14}(OH)_2$	3.47	0.4	>17 GPa	Smyth et al 1997
Wadsleyite II	$Mg_7{}^{IV}Si_4O_{14}(OH)_2$	3.51	0.4 (0.2)	>17 GPa, ~1400°C	Smyth & Kawamoto 1997

[a]See text and figures, for other phases, including muscovite, hydrogarnet, chrysotile, chlorite, and chloritoid.

[b]Silicon coordination in the structure is indicated by IV (tetrahedral) and VI (octahedral); unless otherwise noted, the ideal formula is given.

[c]Includes range of values reported; see cited references, as well as compilations in Ahrens (1995).

[d]Maximum hydrogen content based on stoichiometry is indicated; nominal measured values are given in parentheses.

[e]The bounds give the approximate range of stability, which of course depend on temperature and chemical environment; otherwise, the numbers give maximum pressures and temperatures at which the mineral is stable. The references include citation of the initial characterization of the phase and/or recent studies of the stability range; see also references therein and discussion in the text.

[f]Related iron bearing phases, preliminarily called phase H, have been characterized (see text).

[g]Ideal formula $MgSi_2H_2O_6$; density given for $Mg_{1.11}Si_{1.89}H_{2.22}O_6$ (Yang et al 1997).

[h]Undergoes pressure-induced transitions within this *P-T* range (e.g. Duffy et al 1995; also see text).

[i]Values given for antigorite; broadly similar results are reported for lizardite $[(Mg,Al)_3{}^{IV}(Si,Al)_2O_5(OH)_4]$.

[j]Norbergite, chondrodite, humite, and clinohumite represent the humite series, with stoichiometry given by $Mg(OH,F)_2$ n Mg_2SiO_4; F substitution for OH is particularly significant at lower pressures.

[k]Also includes titanoclinohumite $[Mg_{9-x}Ti_x{}^{IV}Si_4O_{2x}(OH)_{2-2x}]$ (McGetchin et al 1970).

rather completely bound to magnesium ions. These oxygen sites can be viewed as "underbonded" and are particularly amenable to protonation (Smyth 1987). Therefore, the large amounts of water dissolvable in β-phase are a direct (and predictable) consequence of the crystal chemistry of this phase.

Indeed, much as end-member hydrogarnets exist, there is a stoichiometric hydrogen-bearing phase, $Mg_{1.75}SiH_{0.5}O_4$ (or $Mg_7Si_4H_2O_4$), which has been observed to exist in the β-phase structure (Inoue et al 1995). Variable amounts of solid solution between this phase and anhydrous β-phase generate intermediate stoichiometries of hydrated β-phase, and the Mg/Si ratio of the resultant materials can be used to directly constrain the amount of water in the structure. Yet the mechanism of substitution of water into β-phase does not appear entirely straightforward: Recent single-crystal X-ray diffraction studies of hydrous β-$(Mg,Fe)_2SiO_4$ indicate the existence of two different structures in this material (wadsleyite I and II) (Smyth 1994, Smyth & Kawamoto 1997, Smyth et al 1997). The importance of these phases lies not only in their comparatively high water contents, but also in the fact that wadsleyite II has been observed to form within a system of peridotite chemistry: The stability of few high-pressure hydrous phases has been demonstrated in chemically complex systems. The hydrogen positions in these phases were located by X-ray diffraction and were systematically observed to be associated with nonsilicate-bound oxygens in these materials, in accord with the original proposal of Smyth (1987). The deviation of these two phases from the orthorhombic symmetry of anhydrous β-phase may result from the combined ordering of H, Mg/Fe, and Si. From a semantic viewpoint, it is with such different symmetry, yet closely structurally related, phases that the boundary between nominally anhydrous phases containing defect water and crystallographically distinct hydrous phases becomes blurred.

The importance of this hydrous β-phase is not only that it could retain large amounts of water, but also that the difference in water solubility between β-phase and its lower-pressure polymorph could produce release of water from material convectively traversing the 410-km discontinuity, potentially resulting in melting and plume-like upwellings (Young et al 1993). Moreover, the differential solubility in water between the olivine and β-phases could affect the thickness over which the phase transition between these materials occurs at depth: As seismic characterization of the 410-km discontinuity indicates that this transition proceeds over a depth interval (in some locations) of less than about 10 km (Benz & Vidale 1993), and thermochemical analysis indicates that this thickness should provide a strict upper bound of about 200 ppm on the water content of the mantle at this depth (Wood 1995). However, the dissolution of water within β-phase is strongly temperature dependent. Figure 2 shows the amount of water held within β-phase synthesized under a range of temperatures, as derived from the Mg/Si ratios of the resultant materials: At the temperatures relevant to normal (nonsubduction influenced) mantle, it appears likely that less than 0.1 wt% water is soluble within β-phase, and it is possible that for realistic mantle temperatures, β-phase could be essentially anhydrous. Therefore, water present near depths of 400 km may not be sequestered

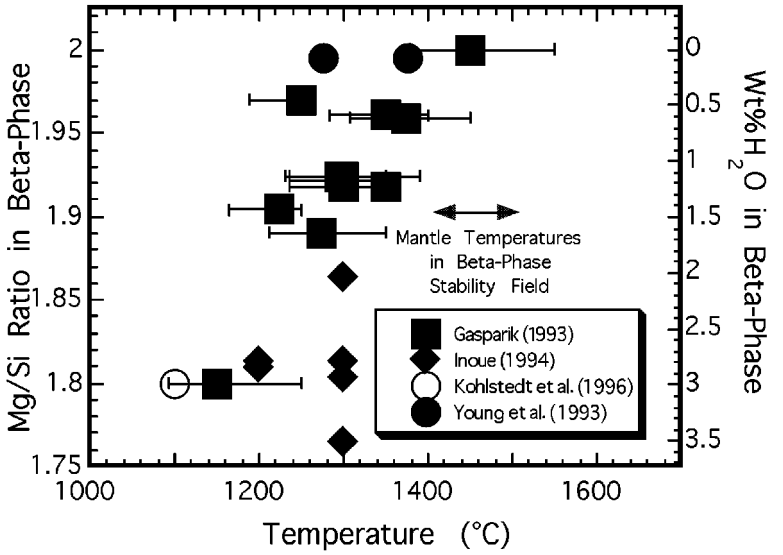

Figure 2 Amount of water in hydrous β-$(Mg,Fe)_2SiO_4$ as a function of temperature, as derived from reported Mg/Si ratios of β-phase within water-bearing charges. Data are from Inoue (1994), Gasparik (1993), Kohlstedt et al (1996), and Young et al (1993). The results of Kawamoto et al (1996) show a similar trend, although their reported temperatures are higher for comparable water contents: This may be a consequence of thermal gradients within their samples. The possible role of changes in crystal symmetry on the temperature dependence of water solubility in this material remains largely unexplored (Smyth & Kawamoto 1977).

within β-phase, rendering estimates of mantle water content based on the sharpness of the 400-km discontinuity only lower bounds on the amount of water at depth.

$(Mg,Fe)_2SiO_4$ γ-spinel has also been observed to retain significant quantities of water at temperatures lower than those of the mantle: 2.7 wt% at temperatures of 1100°C and pressures corresponding to depths near 585 km (Kohlstedt et al 1996, Inoue et al 1997). However, unlike β-phase, essentially no information is available on the temperature dependence of the water dissolution reaction in γ-spinel; neither is there any straightforward crystal-chemical rationale for the manner in which it dissolves water.

Defect Substitution in Lower Mantle Phases At higher pressures, the lower mantle (from 670 to 2950 km deep) is dominated by high-pressure, perovskite-structured phases of silicates and (Mg,Fe)O-magnesiowüstite. The high-pressure silicates in this zone fundamentally differ in their bonding environments from the silicates present in the crust and upper mantle, in that silicon resides entirely in sites with six nearest-neighbor oxygens (octahedral coordination) rather than the fourfold (tetrahedral) sites that predominate at shallower depths. Few data

exist on the solubility of water in such phases, but spectroscopic studies of the higher-pressure mantle phases and their analogs have produced some insights into the mode of incorporation of hydrogen in these materials (Rossman & Smyth 1990, Pawley et al 1993, Lu et al 1994, Meade et al 1994, Li et al 1997, Lu et al 1999). Experiments on analogs of the high-pressure phases include single-crystal neutron studies of hydrogen-containing TiO_2-rutile, which indicate that the hydrogen is located near the shared edge of the cation octahedra (Swope et al 1995), consistent with single-crystal infrared spectra of hydrogen-bearing isostructural SiO_2-stishovite (Pawley et al 1993). Similar arguments based on diffraction and electrical conductivity of perovskite analogs (Beran et al 1996, Kreuer et al 1998, Navrotsky 1999) have been used to understand the crystal chemistry of hydrogen-bearing silicate perovskites (Lu et al 1994, Meade et al 1994). In the case of both perovskite and stishovite, the coupling of hydrogen with aluminum substitution for silicon for charge balance plays a key role in controlling the uptake of the hydrogen (Pawley et al 1993, Smyth et al 1995, Navrotsky 1999).

Yet, as with the upper mantle phases, the absolute amount of water that can be incorporated via defect- or impurity-related substitutions in nominally anhydrous phases is rather small (Meade et al (1994): Magnesium silicate perovskite synthesized under hydrothermal (water-saturated) conditions at temperatures of 1830°C and pressures of 27 GPa (corresponding to depths near 800 km) can incorporate about 0.006 ($\pm$0.0015) wt% water (700 H atoms/10^6 Si atoms). Notably, the temperature at which these synthesis experiments were conducted is compatible with that inferred to be present at the top of the lower mantle. Although the pressure dependence of the solubility of water in silicate perovskite is unknown, magnesium silicate perovskite is plausibly the most abundant mineral in the planet, and even this comparatively small amount of water could produce a reservoir of water retained in nominally anhydrous perovskite of about 12% of the mass of Earth's hydrosphere (Meade et al 1994). Plausibly, this value represents a lower bound on how much water could dissolve in perovskite of the lower mantle as the roles of added aluminum and increased pressures should each be to enhance the solubility of water within silicate perovskite. Indeed, the ability of high-pressure phases containing octahedrally coordinated silicon to retain small quantities of bound water is further illustrated by the observation that rutile-structured SiO_2-stishovite contains about 0.008 wt% H_2O at 1200°C and pressures corresponding to those at depths of 300 km (Pawley et al 1993).

Hydrated Phases Stable at High Pressure

Highly Stable Hydrated Metamorphic Phases Although the importance of amphiboles and micas as possible hydrous phases within the upper mantle has long been appreciated, the past decade has seen a remarkable resurgence in interest in the stabilities of a wide range of well-known metamorphic phases such as talc, zoisite, lawsonite, chlorite, topaz, and serpentine. This interest has been triggered by the recognition that at the relatively low-temperature–high-pressure conditions of subduction zones, several of these phases have stability fields that extend to depths

of 150–300 km. Moreover, phases such as lawsonite, zoisite, and chlorite have been demonstrated to occur in hydrated basalt (Poli & Schmidt 1995, Okamoto & Murayama 1999), whereas topaz could be a major component of subducted pelitic sediments at high pressure (Wunder et al 1993b, Schreyer 1995, Domanik & Holloway 1996). Therefore, these phases could likely represent carriers of water into the deep upper mantle, and the coupling of their dehydration conditions with the geotherms in subducting slabs could be important in determining the pattern of water release from the subducted slab into the overlying mantle (Schmidt & Poli 1998).

Figure 3 shows the pattern of phase stability in hydrated basalt juxtaposed with several mantle geotherms (Poli & Schmidt 1995). Clearly, lawsonite, usually associated with the blueschist facies, has an extremely large stability range within hydrous basalt. Moreover, among mantle-relevant hydrous phases, it is unusual in the amount of water it contains (11 wt%) in its relatively high density (near 3.1 g/cm^3) and in the manner in which it retains water. With a formula of $CaAl_2Si_2O_7(OH)_2{\cdot}H_2O$, it contains water as both hydroxyl ions and as water molecules bound within its lattice: The presence of water molecules within large

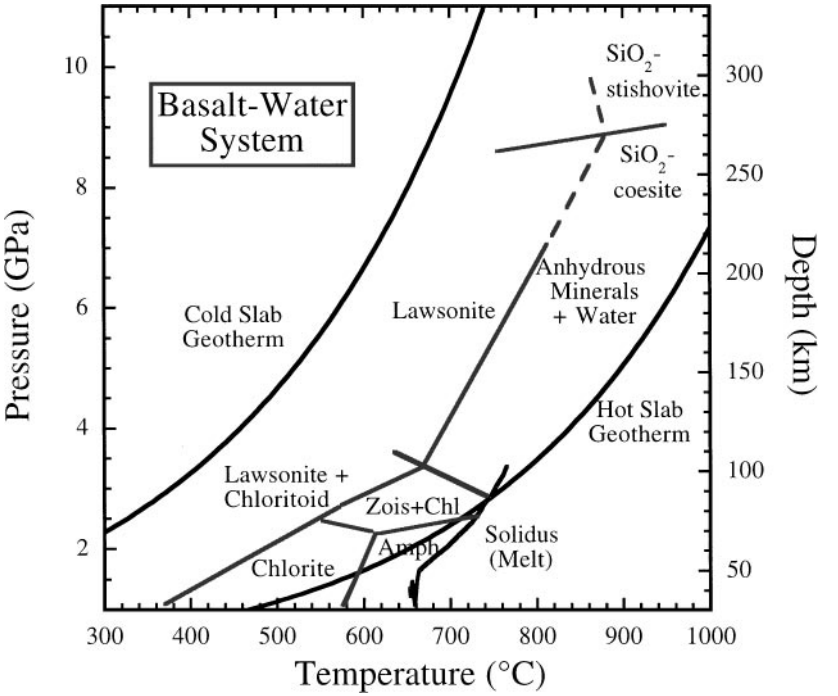

Figure 3 Phase equilibria of the basalt-water system to depths of 330 km (after Poli & Schmidt 1995). Dotted line indicates extrapolated behavior; the shift in slope of the lawsonite decomposition reaction near 9 GPa due to the coesite to stishovite reaction has been observed in both single-phase lawsonite and MORB (Schmidt 1995, Okamoto & Murayama 1999). Hot- and cold-slab geotherms are after Peacock (1990).

cages (shared with calcium ions) is unique among high-pressure hydrous phases (Figure 4).

Therefore, lawsonite is likely particularly efficient at transporting water to depth in subduction zones and has thus been the topic of extensive study. Although lawsonite appears to undergo a structural change near 9 GPa (Scott & Williams 1999, Daniel et al 2000), it does not break down until pressures of 12–13.5 GPa (corresponding to depths of 360–400 km) at temperatures of 800°–960°C (Schmidt 1995, Pawley 1994). Such temperatures (or colder) are likely present in metabasalt subducted to depths near 600 km (e.g. Helffrich et al 1989), and therefore lawsonite could represent a primary carrier of water into the transition zone of Earth's mantle. Indeed, there is some seismic evidence that blueschist-rich assemblages persist to depths of 100–250 km within subducted slabs, based upon the apparent presence of a thin (1–7 km thick), relatively low velocity (minus 5% to minus 7%) layer near the top of northern Pacific subduction zones (Abers 2000).

Serpentine [ideally $Mg_3Si_2O_5(OH)_4$] is likely an important phase in retaining water to depth within subduction zones (Ulmer & Trommsdorff 1995, Wunder & Schreyer 1997, Irifune et al 1998). This phase is generated through hydration of typical mantle rocks and is thus a potential water carrier within any hydrated mantle within subducting slabs. Depending on the degree of serpentinization, mantle material can retain up to 13 wt% water: The magnitude of hydration of oceanic mantle is, however, poorly constrained. The upper pressure limit of the stability range of serpentine has been estimated from as low as 4.4 GPa to above 7 GPa (near 500°C): Its maximum thermal stability is between 650° and 730°C at 2–4 GPa (Ulmer & Trommsdorff 1995, Wunder & Schreyer 1997). Therefore, serpentine could transport water within subducted slabs into the 150- to 200-km depth range: Its dehydration from the mantle portion of the slab could contribute to arc volcanism and/or simply hydrate the overlying basaltic crust, forming lawsonite.

A number of other phases could also play a role in the subduction of water into Earth's mantle: zoisite [ideally $Ca_2Al_3Si_3O_{12}(OH)$] occupies a stability field that could be intercepted by subducted slabs, closing at depths near 90 km (see Figure 3) (Poli & Schmidt 1995, 1998). However, relative to lawsonite, phases such as zoisite contain comparatively little water by weight; as such, they are likely to be minor contributors to the water budget of slabs, although they could have substantial geochemical importance. An additional phase that could play a role in both ultramafic compositions and aluminous pelitic sediments is magnesian pumpellyite [ideally $Mg_5Al_5Si_6O_{21}(OH)_7$]. This phase is stable to pressures of 5–6 GPa and temperatures of 680°–770°C (Artioli et al 1999, Fockenberg 1998, Domanik & Holloway 1996) and appears to be stabilized by calcium- and iron-rich compositions. As such, this phase could be locally important within subduction zones. Additionally, depending on the alkali content of material associated with subducted zones, K-amphibole could be a critically important carrier of water into the mantle: Inoue et al (1998) have documented that K-amphibole is stable to depths of 450 km (~15 GPa) at temperatures below 1200°C. Additional, alkali-rich hydrous phases exist at pressures of 10–17 GPa and temperatures up to 1250°C, but their importance in mantle assemblages is unclear (Luth 1997, Yang & Konzett 2000).

The Al_2O_3-SiO_2-H_2O system is particularly relevant to subducted pelitic sediments and perhaps peraluminous basalts, and several high-pressure hydrous phases exist in this system. At low temperatures (below 400°C), the simple aluminum hydroxide diaspore (AlOOH) is stable to pressures near 6 GPa, with an additional phase "pi" with a stoichiometry of $Al_3Si_2O_7(OH)_3$ being stable to comparable pressures at temperatures to 700°C. Both diaspore and phase pi react with silica near 6 GPa to form fully hydroxylated topaz [$Al_2SiO_4(OH)_2$ (Wunder et al 1993a,b)]. This phase, essentially structurally identical to the low-pressure fluorinated phase, is stable to pressures as high as 11 GPa at temperatures of 1000°C (Wunder et al 1993b, Schmidt et al 1998). At higher pressures, OH-topaz reacts with silica to form a notably thermally stable phase, the so-called phase egg (named after Eggleton et al 1978). This $AlSiO_3OH$ phase has silicon entirely in octahedral coordination: Its upper pressure-stability limit has not been determined (but it is stable to at least 18 GPa), and it has been shown to be stable to at least 1300°C. The crucial aspect of these phases is simply that with these aluminous phases and phengitic micas (Domanik & Holloway 1996), ample phases are available to transport water associated with subducted sediments to depth: The mineral carriers of such water are, however, markedly different from those within the basaltic crust or subducted mantle material.

The possible importance of minerals of the humite family for retaining water at high pressures has long been appreciated (e.g. Akimoto et al 1977). These minerals have the formula $n Mg_2SiO_4 \cdot Mg(OH,F)_2$, in which n values of 2 and 4 correspond to chondrodite and clinohumite, respectively. These minerals have been demonstrated to have stability fields below ~13 GPa and temperatures below ~1000°C in hydrated model mantle assemblages (e.g. Kawamoto et al 1996). Thus, they may be important within the portion of the mantle wedge cooled through its juxtaposition with the subducting slab, or in the subducted oceanic mantle. Additionally, because of their structural similarity to olivine, a portion of the hydrous defects present in "nominally anhydrous" olivine may represent intercalations of these phases (Kitamura et al 1987). The humites have also been proposed to play a role in a "water line" in Earth's mantle, a proposed boundary below which volatiles are stably bound in magnesium silicate assemblages, and above which they are liberated into a fluid (or partial melt) phase. The original concept was that such a line would provide a lower depth limit for the low-velocity zone, with the top being defined by the stability fields of amphiboles or phlogopites (Liu 1987, Ahrens 1989, Liu 1993). Liu (1993) proposed that the reaction $5Mg_2SiO_4 + H_2O = MgSiO_3$ (enstatite) + $Mg_9Si_4O_{18}H_2$ (clinohumite) could produce a "water line" in the mantle. However, although the water-line concept might have utility in anomalously cold and wet regions of mantle, the lack of stability of hydroxyl-clinohumite at the high temperatures of ambient mantle make the global presence of such a water line unlikely.

Dense Hydrous Silicates The idea that water might be sequestered in the mantle within separate hydrous crystalline phases has long had considerable appeal. The key attributes of such phases are that they must be stable within ultramafic assemblages at mantle temperatures and pressures and, in order to be abundant, should

be composed solely of elements that are present in high concentrations within the mantle. These two criteria have proved somewhat difficult to satisfy for all but a few phases. In this section, we focus principally on the so-called alphabet phases, and the closely related humite family of minerals.

Alphabet phases Three decades of experimental studies of hydrous magnesium silicates have demonstrated the existence of a number of hydrous phases with stabilities corresponding to depths much greater than 200 km. Figure 5 shows a ternary diagram that shows the compositions of various hydrous magnesium silicates. Proposed dense hydrous magnesium silicates (DHMS) include the 10-Å phase (Sclar et al 1965); the 3.65-Å phase (Sclar et al 1967); phases A, B, and C (Ringwood & Major 1967); phase D (Yamamoto & Akimoto 1974); phase D' (Liu 1987); phase E (Kanzaki 1989, 1991); phase F (Kanzaki 1991), and anhydrous B and superhydrous B (Gasparik 1990, 1993). Crystal structure refinements have been reported for phases B (and anhydrous B) (Finger et al 1989, 1991). Apparently, the crystal structures of the 10-Å or 3.65-Å phases have not been determined; in fact, only Sclar et al (1967) have reported the existence of the latter

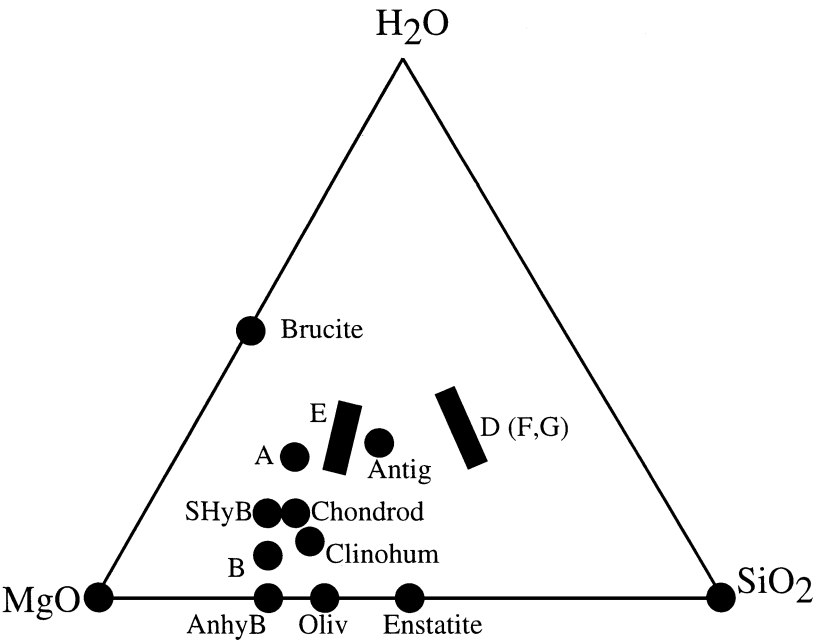

Figure 5 Ternary diagram illustrating compositions of important high-pressure hydrous phases in the MgO-SiO_2-H_2O system. The boxes labeled *E* and *D* show ranges of compositions observed for these phases; letters in parentheses indicate additional names that have been used for these phases.

phase. The structure of the 10-Å phase is thought to be similar to that of talc (see Prewitt & Parise 2000). The "phase B series" structures are related to the humites (and ultimately olivine) by simple crystallographic shear (Pacalo & Parise 1992). Recent studies of the Fe-bearing system have uncovered related, but new, structure types; this includes phase H, which is related to phase E (CT Prewitt, H Yang, in preparation).

There has been considerable confusion over the nomenclature and identification of these materials because of the multiphase and/or very fine-grained nature of the samples and problems with interpreting diffraction patterns. For example, recent work has shown that phase C (Ringwood & Major 1967) is probably identical to superhydrous B (Pacalo & Parise 1992). Yamamoto & Akimoto (1974) first proposed phase D, but this material turned out to be chondrodite, one of the humite series. However, the phase D identified and characterized by Liu (1987) was confirmed. It has the same crystal structure as that of phase G reported by Kudoh et al (1997a). Kanzaki (1991) described a putatively new material called phase F, but it actually appears to be phase D; Kudoh et al (1994) also identified a phase F, but this turned out to be phase C, now called superhydrous phase B (Kudoh et al 1997b).

Beyond the intrinsic crystal-chemical interest of the variety of hydrated phases (cf Table 1), the primary geophysical importance of these hydrated phases naturally lies in whether or not they are actually stable at the pressures, temperatures, and chemistries present within the mantle. In this regard, it is notable that the vast majority of studies of DHMS have been conducted in compositionally simple systems, with most of these being conducted in the MgO-SiO_2-H_2O ternary system. Nevertheless, a number of conclusions can be drawn about the importance of these separate phases within the mantle. For example, Table 1 shows both materials whose highest temperature of stability lies below $\sim$1000°C, and those with higher temperature stabilities. Accordingly, most of the hydrous phases discovered to date have too limited a range of thermal stability to be present within the bulk of the mantle. Nevertheless, a number of these lower-temperature phases could be stable within subduction zone environments.

The structural behavior of hydrogen in these phases has been addressed with the combination of single-crystal X-ray diffraction and vibrational spectroscopy. The structure of phase E determined under ambient conditions is very unusual in that it is characterized by long-range disorder but its single-crystal diffraction pattern shows sharp spots with no evidence of disorder (Kudoh et al 1989, 1993, Crichton & Ross 2000). Liu et al (1997b) described phase E as the hydrous form of forsterite. The issue of whether quenched phase E has the same structure as it does under the original synthesis conditions prompted in situ X-ray diffraction studies. The powder diffraction pattern of the temperature-quenched sample at high pressure is identical to the low-pressure structure, which suggests a similar structure at high *P-T* conditions (Shieh et al 2000b). However, additional in situ high *P-T* measurements are needed to fully examine the possiblity of temperature-quench effects. The recently proposed phase H appears in the *P-T* stability range

of phase E and seems to be a related structure type, as mentioned above: These phases have interlinked magnesium octahedra and silica tetrahedra in a layered arrangement, but with a complex vacancy structure within the layers (Figure 4). These vacancies produce the nonstoichiometry of this phase, as illustrated by the bar in Figure 5. One of the key aspects of phase E is that it may have a stability field that extends to about 1100°C at 12–15 GPa (Inoue 1994), indicating that it could be a host for water in subduction zones at significantly higher temperatures than such phases as lawsonite.

Phase D is potentially the most important of these materials because it has the highest pressure stability of any phases observed in the family of dense hydrous magnesium silicates and, thus, could represent the major means by which water is sequestered at depths between 600 and 1250 km in the mantle. The infrared reflectance spectrum shows that only SiO_6 structural units (near 700 cm^{-1}) are present, with no evidence for SiO_4 tetrahedra (expected between 1000 and 1500 cm^{-1}), typical of crustal and upper mantle silicate minerals. This was subsequently confirmed by single-crystal X-ray diffraction (Yang et al 1997). Moreover, the vibrational spectra reveal variable hydrogen bonds, with a low hydroxyl frequency at ~2850 cm^{-1}, corresponding to an $OH^{\cdots}O$ bond length of 2.67 Å (Novak 1974), later found in the X-ray structure refinement (Yang et al 1997). The degree of compression of the short oxygen-oxygen distance in phase D [$r(O\text{-}H^{\cdots}O) = 2.67$ Å] is estimated to decrease to 2.54 Å at 30 GPa and to 2.51 Å at 50 GPa, which suggests the existence of very anharmonic and possibly diffusive behavior of the protons at high *P-T* conditions prior to breakdown. Both the structure and equation of state of phase D depend on Fe content (Shieh et al 2000a), although how this may couple with possible nonstoichiometry with respect to the hydrogen remains to be explored. Overall, the structure of this phase is notably simple (Figure 4), with the silicon-bearing layers in the structure similar to those present within $Mg(OH)_2$-brucite (Yang et al 1997).

The phase relations of the high-pressure hydrous silicates have been reviewed by Frost (1999) (see also Gasparik 1993, Bose & Navrotsky 1998, Angel et al 2001). Combined laser-heating/in situ X-ray diffraction experiments show that like phase E, superhydrous B and phase D are indeed stable at high *P-T* conditions and are quenchable to ambient conditions (Shieh et al 2000a). Superhydrous phase B is stable to pressures at the bottom of the transition zone and top of the lower mantle (Figure 6), and may be stable to temperatures near those of the geotherm in the deeper portion of the transition zone (e.g. Gasparik & Drake 1995). The high pressure-temperature stability of phase D ($Mg_{1.11}Si_{1.89}H_{2.22}O_6$) has been the subject of several studies (Ohtani et al 1997; Frost & Fei 1998; Irifune et al 1998; Shieh et al 1998, 2000a). Phase D has been shown to be stable to lower mantle conditions (Frost & Fei 1998, Ohtani et al 2000) and reported to coexist with silicate perovskite and stishovite (Li & Jeanloz 1991). High *P-T* diffraction experiments show that the phase decomposes above 50 GPa and 2100 K, releasing H_2O at higher *P-T* conditions (Shieh et al 1998). This indicates that if phase D passes the "choke" point in slabs (geotherms cool enough to avoid the free H_2O and melt

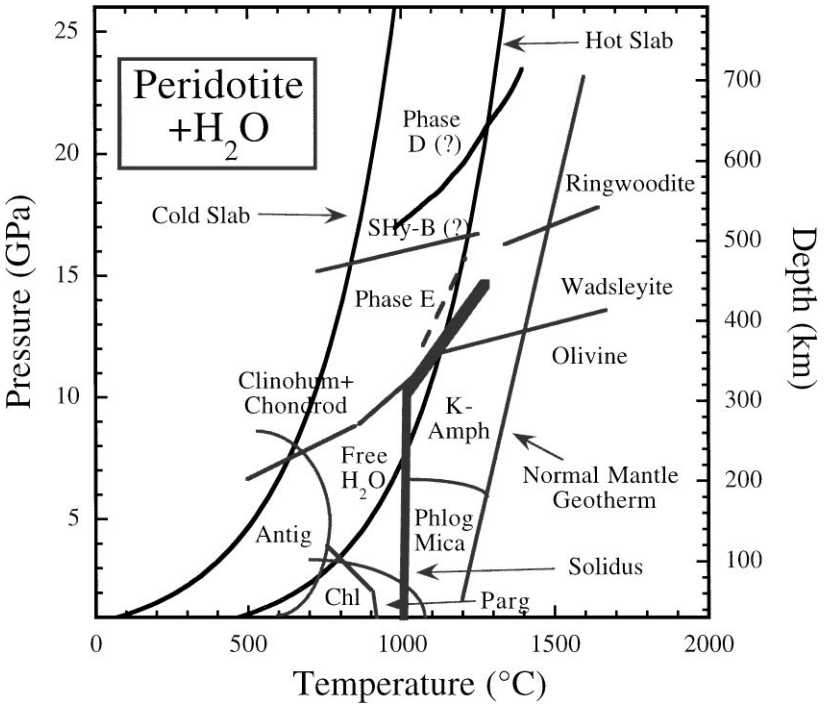

Figure 6 Stability diagram for hydrous phases as a function of pressure and temperature for a peridotite mineralogy. Lower-pressure region (below 15 GPa) is modified after the data and compilations of Kawamoto et al (1996) and Kawamoto & Holloway (1997). Higher-pressure data on superhydrous B and phase D is inferred based on phase equilibria of serpentine and olivine plus water compositions (after Shieh et al 1998, Frost & Fei 1998). Par denotes pargasitic amphibole and chl indicates chlorite. Notably, the water retention in K-amphibole and phlogopite is small, as the modal abundance of these phases is limited by the potassium content of the mantle (O $\sim$ 0.1 wt%). Slab geotherms are from Peacock (1990).

fields in Figure 6), it would persist to a depth of $\sim$1250 km before dewatering, possibly defining the lower depth limit for stability of stoichiometric dense hydrous silicates. Thermodynamic calculations based on the recently measured equation of state indicate that phase D is only marginally denser than the high-temperature dehydrated assemblage at 30 GPa (Frost & Fei 1999). There is some evidence for the existence of additional (nonquenchable) dense hydrous phases, but further work is required to characterize them (Shieh et al 2000a).

That phases such as phase B and superhydrous B have Mg/Si ratios greater than 2 has generated speculations that these phases might not be stable within a peridotitic mantle assemblage with an Mg/Si ratio near 1.3 (e.g. Smyth 1994). Yet, it is a trivial observation that phases with elemental ratios that differ from

the bulk chemistry of a system (as, for example, the Al/Mg ratio in garnets in peridotite) are stable. The crucial question is whether an assemblage containing hydrous phases is stable relative to forsterite and water. Indeed, it has been shown that at temperatures below 1200°C, phase B and/or superhydrous B can be formed from materials with Mg/Si ratios in the 1.5–2.0 range (Gasparik 1993, Pacalo & Parise 1992, Ohtani et al 1995). Similarly, phase E (with an Mg/Si ratio close to 2) has been shown to form from olivine and water (Inoue 1994, Ohtani et al 1995, Frost & Fei 1998). Therefore, there appears to be no significant compositional impediment to the formation of these phases within mantle assemblages.

Role of additional elements in DHMS phase stability The role of major elements such as Ca, Al, and Fe in stabilizing or destabilizing hydrous high-pressure phases is particularly poorly understood; the effect of other minor elements is entirely unknown. In one of the few detailed studies of the effect of additional components on hydrous phase stability, Luth (1995) has shown that the stability field of phase A is decreased relative to the pure MgO-SiO_2-H_2O system by the presence of calcium (by 70°–120°C at 8 GPa), aluminum (by 40°–80°C), and iron (by ~20°C) and is unaffected by CO_2 content.

However, as with amphiboles and micas, it appears that the thermal stability of DHMS phases notably increases with halogen content. The substitution of fluorine for hydroxyls appears to enhance the stability of superhydrous B and phase E by over 100°C (Gasparik 1993): The fluorinated versions of these phases have stabilities that approach 1500°C at 15 GPa, or essentially the conditions of ambient mantle. The importance of this observation is simply that upper mantle micas and amphiboles typically have 0.4–1 wt% fluorine (Smith & Dawson 1981), and comparable levels of halogens would be expected to markedly stabilize hydrous phases.

Metastability of hydrous phases? The plethora of hydrous phases with subtly differing (and sometimes variable) chemistries and densities raises the fundamental question of which of these phases are thermodynamically stable. Indeed, the occurrence of extensive metastability has been known in the MgO-Al_2O_3-SiO_2-H_2O system even at low pressures for decades (e.g. Yoder 1952). Among the phases of Table 1, the 10-Å phase, partly because of its comparatively low pressure and temperature stability range, has been subjected to perhaps the most intense scrutiny of its (meta)stability. This phase has been proposed to lack any thermodynamic stability field based upon the fact that it breaks down to form talc in charges of its precise chemistry at conditions that span its proposed stability field (Wunder & Schreyer 1992). This conclusion has been questioned by Pawley & Wood (1995), who observed the reaction of talc with excess water to form the 10-Å phase at pressures above 5 GPa. The crucial aspect of this discrepancy is simply that the generation of hydrous phases in excess water-bearing synthetic systems need not be associated with a thermodynamic stability field of the phase (particularly for syntheses done at relatively low temperatures): Nucleation of metastable phases

in such systems is well-known (Yoder 1952). Additionally, the observation of an (even if stable) hydrous phase in synthetic simple systems certainly does not indicate that it will occur in natural systems. For example, the large stability field of lawsonite in basaltic compositions plausibly obviates the necessity of invoking the presence of the 10-Å phase, phase A, or talc within subducted basaltic crust. The conclusion that phase A and talc might be relatively unimportant in water transport in the upper mantle is in accord with experiments on the stability range of phase A in complex assemblages (Luth 1995) and with field observations and petrologic constraints on the lack of occurrence of talc in high-pressure ultramafic assemblages (Liou & Zhang 1995).

There are two other instances in which metastability could be of significant geologic importance in understanding the behavior of hydrous phases. If a given subduction zone is sufficiently cold that the kinetic barriers to dehydration are prohibitive, then nominally unstable hydrous phases might be carried to depths well beyond their formal thermodynamic stability fields (e.g. Scott & Williams 1999, Daniel et al 2000). Yet few data are available on the kinetics of hydrous phase decomposition. Serpentine has been examined at high pressures and low temperatures, demonstrating that it is destabilized on the laboratory timescale at temperatures above $\sim$400°C (Irifune et al 1996, Kuroda & Irifune 1998). Many other hydrous phases persist at 300 K to pressures vastly beyond their nominal low-pressure stability field (Williams 1992, Scott & Williams 1999), although in some cases amorphization transitions may intervene (Kruger et al 1989, Meade & Jeanloz 1991). However, the thermal stability of such amorphous phases is likely limited (Irifune et al 1996, Kuroda & Irifune 1998), and they may not occur within the Earth.

An additional aspect of metastability in hydrous systems explains why few, if any, of the so-called dense hydrous phases are likely to be observed in xenoliths. Phases A, B, and D have been observed to rapidly decompose or amorphize at ambient pressure at 440°C, 300°–400°C, and 100°C, respectively (Liu et al 1997a, 1998a,b). Accordingly, although these phases could conceivably persist during ascent or emplacement from depth as a microinclusion within diamond, the likelihood of their being found in a xenolith is minimal. Therefore, the possible existence of these phases within the interior of the planet is likely to remain inferential.

Elastic properties of DHMS The densities of the hydrous phases are grossly similarly to those of the phases of the upper mantle and transition zone; most hydrous phases have bulk moduli that are also generally within $\sim$10% of that of the $(Mg,Fe)_2SiO_4$ polymorph with a similar stability field (Figure 7). Some effects on the elastic properties of hydrous phases (in comparison with their anhydrous counterparts) are significant. The presence of hydrogen in ringwoodite (estimated composition of $Mg_{1.89}Si_{0.97}O_4H_{0.33}$, or 2.2 wt% water) lowers its elastic moduli by $\sim$10% and produces compressional and shear wave velocity decreases of 5.3% and 3.6%, respectively. The material also becomes more elastically anisotropic (Inoue et al 1998).

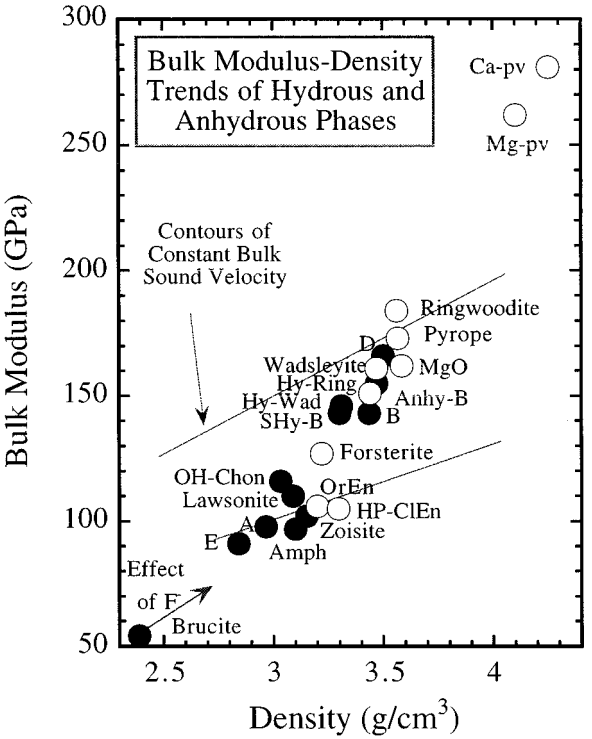

Figure 7 Trends in bulk modulus versus density for hydrous (solid circles) and anhydrous mantle phases (open circles). Data from Angel et al (2001), Knittle (1995), and Bass (1995). Amph denotes amphibole and represents values for pargasite and glaucophane, HP-ClEn indicates the high-pressure clinoenstatite-structured phase of $MgSiO_3$, OrEn is orthoenstatite, and pv is perovskite. The vector pointing from brucite describes the possible effect of substituting fluorine on the elastic properties of hydrous phases: It indicates the direction of change in bulk modulus and density on going from $Mg(OH)_2$ to MgF_2 (which has a density and bulk modulus comparable to zoisite). Contours represent isopleths of constant bulk sound velocity: Clearly, such low-pressure hydrous phases as lawsonite and zoisite will be seismically resolvable if juxtaposed with an olivine-pyrope dominated mantle. However, phase D is not readily distinguishable from MgO in the lower mantle, or from wadsleyite in the deep transition zone.

Few shear moduli of hydrous phases are available. However, the shear moduli of chondrodite and clinohumite lie within 5% of that of olivine (Fritzel & Bass 1997, Sinogeiken & Bass 1999). Therefore, from the perspective of seismic wave velocities, discerning the amount of water within the upper mantle or transition zone would be feasible only if the mantle comprised on the order of tens of percent of a dense hydrous phase (e.g. Faust & Knittle 1994, Fritzel & Bass 1997). This implies a seismic detection limit of $>\sim$2 wt% water in the upper mantle, and perhaps $>\sim$1 wt% in the deep transition zone, if the velocity contrasts associated

with hydrous ringwoodite persist to high pressure. Given that the MORB source region has ~125 ppm water (0.01 wt%), it appears that seismic probes will be unable to resolve the presence of hydrous phases within the bulk of the upper mantle. Similarly, although phase D does have elastic properties that diverge significantly from the magnesium silicate perovskite phase that dominates the lower mantle, its bulk modulus is similar to that of magnesiowüstite. Therefore, resolving the presence (or absence) of phase D in the lower mantle is likely to be difficult, unless its shear modulus markedly differs from that of major lower mantle phases (Figure 7). Finally, the effects of iron, calcium, aluminum, or halogen content on the elastic properties of the hydrous phases (as well as the effects on phase equilibria) are almost completely unexamined, although there are indications that fluorine could have a significant effect (Figure 7).

Effects of Water on Transport Properties

It has been known for several decades that small quantities of hydrogen (100 ppm level) can greatly influence the strength and electrical conductivity of minerals at low-pressure conditions (e.g. Kats 1962, Griggs 1967). As a result, numerous dielectric and rheological studies of hydrogen-bearing minerals have been carried out over a range of *P-T* conditions (e.g. Chopra & Paterson 1984, Karato et al 1986, Mackwell & Kohlstedt 1990, Li & Jeanloz 1991, Weidner et al 1994, Karato 1995, Hirth & Kohlstedt 1996, Sweeney 1997, Chen et al 1998). These studies point to the important relationship between chemical environment, defect concentration, and the nucleation and migration of dislocations that control the dramatic changes in transport properties induced by the presence of hydrogen.

Fortunately, the transport properties of olivine are among the best studied of any geologic material. Indeed, for olivine, even samples with approximately 100 hydrogen ions per 10^6 Si (~6 ppm water) have been demonstrated to be approximately a factor of two weaker than "dry" samples (Mackwell et al 1985). For higher water contents in olivine at 1.7 GPa (50 ppm, or approximately half the saturation limit of olivine at this pressure, and an amount compatible with 125 ppm water within the MORB source region), the viscosity of granular olivine (or olivine rock) is more than two orders of magnitude less than that of dry olivine (see Figure 8) (Hirth & Kohlstedt 1996). Similarly, although no direct measurements exist on the effect of minor amounts of dissolved hydrogen on the electrical conductivity of olivine, calculations based on the rate of hydrogen diffusion in this phase indicate that 100–1000 hydrogen ions per 10^6 Si atoms (6–60 ppm water) may elevate the electrical conductivity of the upper mantle by one to three orders of magnitude (Karato 1990). Such a hydrogen-induced enhancement of conductivity could explain the relatively high conductivity near the top of the asthenosphere (depths of ~90–150 km) without invoking the presence of partial melt at these depths (Karato 1990). Indeed, forward modeling indicates that the presence of a high-conductivity pathway associated with hydrogen diffusion is likely required throughout the upper mantle to match magnetotelluric sounding results (Farber et al 2000).

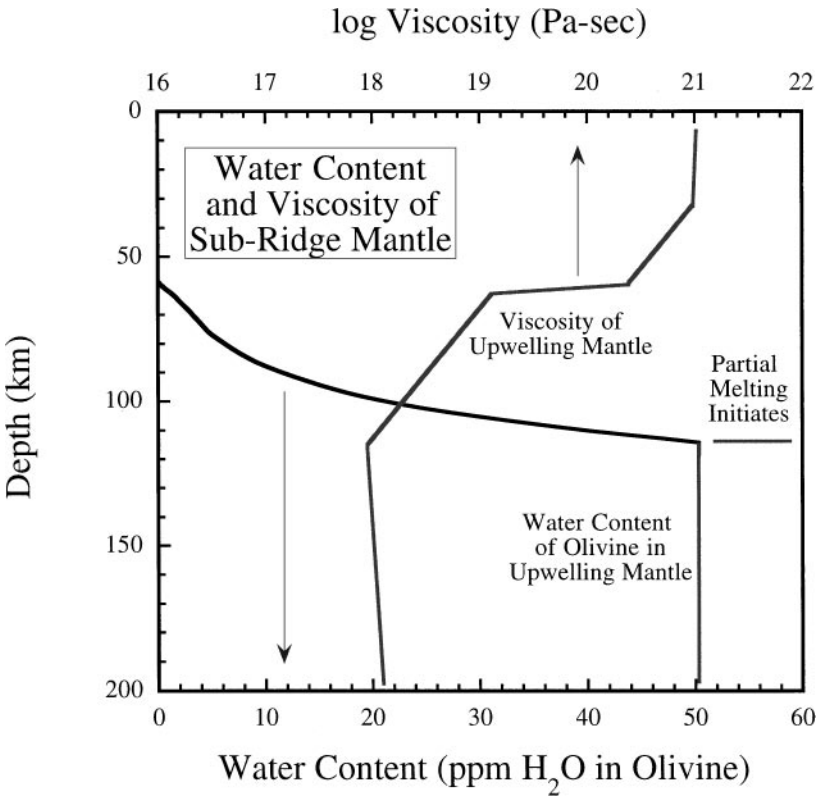

Figure 8 Change in the viscosity and water content on upwelling and partial melting of subridge mantle (after Hirth & Kohlstedt 1996). The change in viscosity at depths shallower than ~65 km is produced by melting-induced temperature changes within the upwelling mantle.

The dramatic effect of water on the strength of olivine is probably produced by larger rates of dislocation climb within hydrogen-bearing samples. This may be produced by hydrogen within the dislocation core either (*a*) enhancing the ability of the dislocation to glide and climb or (*b*) reducing the number of kinks and jogs associated with dislocations (e.g. Mackwell et al 1985). Not only does the absolute strength of olivine-dominated rock vary with water content, but the flow law, the dependence of strain rate on stress as a function of temperature, changes as well. Accordingly, the extrapolated behavior of wet olivine at conditions of the mid-upper mantle differs more from the inferred properties of dry olivine than from those measured at low-pressure conditions. Unfortunately, among mantle minerals, olivine is unique in having had its rheology closely examined under both dry and hydrated conditions. Extrapolations of wet flow behavior are thus largely limited to upper mantle conditions.

Beyond its intrinsic material interest, the role of water in drastically lowering the viscosity of silicate rock likely has important geodynamic consequences as well. Because of the strong partitioning of water into melts, upwelling (and mildly hydrated) mantle that begins to partially melt on ascent will rapidly and efficiently have most of its water content stripped into a low-degree partial melt, leaving behind a strong, mostly dehydrated residual solid. This dehydration-induced strengthening has been invoked as a primary cause of the narrow upwelling zone beneath ridges, as the dehydrated mantle is sufficiently viscous that it can maintain lateral corner-flow pressure gradients capable of focusing melt into a narrow ridge axis (Hirth & Kohlstedt 1996, Braun et al 2000).

There is a notable paucity of studies on the effect of water on the transport properties of the high-pressure phases of the transition zone and lower mantle. Electrical conductivity studies on an assemblage of $(Mg,Fe)SiO_3$-perovskite and phase D–containing 4 wt% H_2O showed an increase of approximately three orders of magnitude relative to an anhydrous assemblage at pressures of 48–57 GPa (Li & Jeanloz 1991). In terms of deformation, studies of the yield strength of the higher-pressure phases of olivine at 10–20 GPa indicate that the drop in yield strength of hydrated olivine is almost a factor of two larger for the olivine phase (α phase) than for the β and γ phases (Chen et al 1998). Although this study was only conducted to 400°C, a principal conclusion is that the manner in which hydrogen is incorporated into the crystal structure, rather than just the amount of hydrogen present, may play an important role in controlling the weakening of these materials. Kubo et al (1998) found that the growth rate of β-phase wadsleyite from olivine is significantly enhanced by H_2O. H_2O also increased the rate of dislocation recovery, and Kubo et al (1998) observed that wadsleyite can be weakened by water contents as low as 0.05 wt%. On the other hand, Chen et al (1998) found little effect on the deformation on this material on the basis of X-ray line broadening, albeit at lower temperatures (600°C) and 10 GPa.

Mantle Fluids at High P-T Conditions

Evidence for the existence of hydrous fluid phases in the mantle has been derived from a broad range of probes. These include the presence of fluid inclusions in a wide range of xenoliths (Andersen et al 1984, Navon et al 1988, Turner et al 1990, Schrauder & Navon 1994), geochemical and mineralogic evidence for metasomatic alteration of mantle materials by hydrous fluid phases (e.g. Agrinier et al 1993, Dyar et al 1993), the oxygen fugacity of mantle-derived assemblages that may be buffered by fluid phases (e.g. Wood et al 1990), and seismic evidence for partially molten zones lying in the 300- to 400-km depth range within the upper mantle (Revenaugh & Sipkin 1994, Nolet & Zielhuis 1994). Indeed, Thompson (1992) has emphasized the importance of hydrous silicate melts as a major water reservoir within the mantle. This is simply a consequence of much of the upper mantle and transition zone lying above the temperature of the wet solidus, coupled with the likely neutral buoyancy of silicate melts at deep upper mantle depths (Rigden et al

1988). Indeed, the few experimental data available suggest that hydrous silicate melts may access extremely high densities at deep lower mantle conditions as well (Tyburczy et al 1991). Therefore, small amounts of hydrous melts could have an effectively infinite residence time within the deep upper mantle, transition zone, or lower mantle. Moreover, the large solubility of water within silicate melts at deep upper mantle pressures [well over 10 wt% (Closmann & Williams 1995)] could lead to low-degree (O $\sim$ 0.5%) partial melts containing larger net water contents than can exist within nominally anhydrous phases.

The distinction between a free hydrous fluid phase and hydrated silicate melt may not be operative at deep mantle conditions. There are indications that hydrated silicate melts and hydrous fluids may become fully miscible at upper mantle conditions (Shen & Keppler 1997). In any case, the solubility of silica in hydrous fluids at even deep crustal conditions is above 10 wt% (e.g. Manning 1994). The role of hydrous melting may also play a role in determining the mineralogy of the mantle: Melting relations in hydrous primitive mantle compositions (to 6.5 GPa) indicate that the stability field of orthopyroxene expands relative to that of olivine (Inoue & Sawamoto 1992, Ohtani et al 1996, Asahara et al 1998). Indeed, Ohtani et al (1996) proposed that cratonic peridotites formed as residues of partial melting with variable H_2O contents at depths of about 200 km.

The deepest depth to which hydrous fluids have been demonstrated to exist is derived from fluid inclusions within diamonds. Hydrogen is observed in diamond both in its structure (e.g. CH defects) and as a component in macroscopic inclusions (solid or fluid). Recent infrared studies of cuboid and fibrous diamonds have been shown to contain H_2O (Schrauder & Navon 1994, Kagi et al 2000). Moreover, a comparison between temperature-dependent spectra of compressed H_2O and cuboid diamonds indicates that ices VI and VII are present as inclusions at confining pressures of about 2 GPa (Kagi et al 2000). This may be compared with the similar observation of pressure-solidified CO_2 contained in diamond at room temperature (Schrauder & Navon 1993). Such fluid inclusions within at least some diamonds provide prima facie evidence for the presence of hydrous fluids within their source regions, at pressures greater than $\sim$5 GPa (corresponding to depths of $\sim$150 km). The role of hydrous fluids in the formation of the diamonds themselves remains enigmatic.

Free water (certainly impure) is likely to occur only under exceptional conditions in the mantle: within and directly above dehydrating subducting slabs, and perhaps at pressures and temperatures that lie above the stability field of nonalkalic amphiboles ($>\sim$3 GPa, or 90 km depth) in subcontinental mantle (e.g. Watson et al 1990). Indeed, it has even been suggested (Bina & Navrotsky 2000) that ice VII, an unquenchable phase, might be stable in the coolest regions of subducted slab. In the shallow upper mantle, a carbonate or CO_2-rich fluid containing some water is generally expected from melting peridotite or lherzolite containing small quantities of water and carbonates (Olafsson & Eggler 1983, Wallace & Green 1988). If free water were present, it would be expected to have a significant magnetotelluric signature. The electrical conductivity of water

increases dramatically at the *P-T* conditions of the mantle (and core) and is consistent with the presence of proton carriers (Chau et al 1999); the results are close to theoretical predictions (Cavazzoni et al 1999).

HYDROGEN IN THE CORE

Shortly after the proposal that molecular hydrogen should breakdown to a non-molecular, metallic modification at very high pressures (Wigner & Huntington 1935), it was suggested that dense hydrogen could be a dominant component of the Earth's core and that the core-mantle boundary may coincide with the pressure-induced dissociation transition (Kronig et al 1946). Birch (1952) showed that a large hydrogen component was untenable on the basis of its presumed low density even in the hypothetical metallic state. Dissolution of hydrogen into the core received renewed consideration some 25 years later (Stevenson 1977), but the possibility received little attention because of the very limited solubility of hydrogen in iron at atmospheric pressure (i.e. Stevenson 1981). However, Antonov et al (1980) showed that the affinity of hydrogen and iron increases significantly with pressure such that a stoichiometric iron hydride can be formed at high pressure. This led to a third period of interest in hydrogen in the core, including a study of the water-iron reaction (see below) as a model reaction in the primordial Earth (e.g. Fukai 1984, Suzuki et al 1984, Sugimoto & Fukai 1992), and the observation of the substantial freezing point depression of iron in the presence of hydrogen (Suzuki et al 1984). Subsequent studies of the Fe-H system, including in situ structural investigations (Somenkov et al 1987, Badding et al 1991) and high *P-T* melting experiments, were carried out in the following decade (Okuchi 1997, 1998).

Iron Hydride

By pioneering neutron diffraction measurements, Somenkov et al (1987) showed that stoichiometric FeH forms from hydrogen and iron, crystallizing in the double hexagonal close packed structure near 3 GPa and remaining stable to at least 35 GPa (at room temperature). Subsequent in situ X-ray diffraction experiments by Badding et al (1991) revealed that FeH is stable to at least 60 GPa (at room temperature). Moreover, it becomes more stable relative to Fe and H_2O (Badding et al 1992). There is a 17% expansion of the unit cell in the double hexagonal close packed structure relative to that of (hcp) ε-Fe.

High-temperature studies have been restricted to lower pressures and largely to quenching experiments. The surface tension of molten iron hydride as a function of temperature (at 5 GPa) is much higher than that of silicates, indicating that gravitational separation of molten iron occurs when the degree of melting is very high (Hishinuma et al 1994). Yagi & Hishinuma (1995) carried out in situ high *P-T* X-ray diffraction measurements on the iron-enstatite-water system over a similar range and showed that above 2.8 GPa and 550°C, iron reacts with water to form iron hydride. They estimated the composition of the hydride at these conditions

to be $FeH_{0.3}$-$FeH_{0.4}$. Comparison with the reaction pressure of 3.5 GPa at room temperature (Badding et al 1991, 1992) suggests a negative *P-T* boundary for the transformation. The melting temperature of FeH_x was found to have a minimum at 3–4 GPa, some 600°C below that of pure iron.

Indeed, iron is known to react with water via two primary oxidation reactions. Depending on the pressure, these are

$$MgSiO_3 + Fe + H_2O \rightarrow (Mg,Fe)_2SiO_4 + H_2 \quad (1)$$

and

$$3Fe + H_2O \rightarrow 2FeH + FeO. \quad (2)$$

Reaction 1 is expected at low pressures and clearly annihilates water, with the resultant hydrogen presumably either escaping from the upper atmosphere or reacting with other material, such as carbon (Ringwood 1979, Lange & Ahrens 1984). Reaction 2 occurs at pressures above ~5 GPa (Suzuki et al 1984): The resultant FeO may react with silicates or descend with the FeH into the Earth's core.

The uptake of H in liquid Fe under pressure increases with temperature (Fukai 1993, Okuchi 1997). Okuchi (1997) measured the hydrogen content in molten iron at 7.5 GPa and determined the hydrogen partitioning between silicate and iron melt as a function of temperature. According to this study, in a hydrous magma ocean, >95% of the H_2O should have reacted with Fe to form FeH and 60% of the density deficit of the core can be accounted for with hydrogen as the light element. The sequestered H in this scenario requires no additional light elements for matching the density deficit for the core, including that of the inner core (see also Badding et al 1991, 1992). Okuchi (1997) further assumed a model composition with 2% H_2O (Ringwood 1977), with 95% of the H_2O consumed at temperatures above the dry solidus (~1800°C). At lower temperature, the silicate crystallizes and all the H is consumed to form FeH. Thus, the iron hydride–forming Reaction 2 could effectively help dry out the silicate mantle in the primordial Earth. Moreover, accreted H_2O dissolved in the magma ocean (and not volatilized by subsequent impacts) will further dissolve in any ponding at the base of a magma ocean (Stevenson 1990a). Increasing pressure and temperature further stabilizes FeH (in the above reactions), so the hydrogen in the iron does not return to the silicate at greater depth (i.e. during descent of the metal phase).

Hydrogen and Other Light Elements

Okuchi (1997) further examined the role of sulfur and carbon in combination with hydrogen using Ringwood's two component composition model (Ringwood 1977). An H/Fe ratio of 0.41 yielded a 5.5% density reduction, with 1.1% due to sulfur and 2.2%–2.7% due to carbon, for a total density reduction of 9%, which matches the observed density deficit for the outer core. Moreover, if H/Fe reaches

0.34, as proposed, this would reconcile about two thirds of the inner core deficit. This is broadly compatible with analysis of density profiles through the inner core based on the measured equation of state of FeH core (Badding et al 1991, 1992). Very recent data on Fe_3C bear on this issue (Li et al 2000, Scott et al 2001; see also Jana & Walker 1999).

This analysis ignores the possible presence of oxygen in the core. Moreover, it was based on measurements conducted at 7.5 GPa; pressure effects are likely to change these estimates, particularly at the more extreme conditions of the base of a possible magma ocean (>25 GPa) and at core pressures (>135 GPa). It is notable that such models for core formation assume relatively oxidizing conditions, in contrast to multistage geochemical models that have Si and S as light elements and require extremely reducing conditions. In the latter, the core becomes progressively more oxidized as S is incorporated and iron is oxidized and goes into silicates (Allegre et al 1995; see also Wood 1997).

One of the most profound effects of the presence of hydrogen is on the thermal state of the interior. For example, a composition of $FeH_{0.34}$ melts some 600 K below iron at 5 GPa [decreasing at a rate of $1.8\,(0.2) \times 10^3$ K per mol fraction of hydrogen], for a freezing point depression of over 25%. A portion of the marked effect of hydrogen on the iron-melting temperature is simply associated with its low atomic weight: The number of moles of hydrogen that may be present in the outer core far exceeds those of other possible lighter alloying components (e.g. Williams 1998). Estimates of temperatures at the top of the core range from 3900–4500 K, with the temperature drop across D'' and the core-mantle boundary being $\sim$1300 K. Assuming a range of possible temperature profiles through the mantle (i.e. based on phase equilibria data), the proposed thermal boundary layer at the base of the mantle could be reduced from 1300 K to perhaps <500 K (i.e. Okuchi 1998, Williams 1998).

Thermodynamic calculations suggest that the solubility of hydrogen in iron is only weakly temperature dependent at higher pressures (Sugimoto & Fukai 1992). The nature of the solid at the highest temperatures, including the crystal structures and degree of hydrogen incorporation, is not clear; indeed the equilibrium solubility of hydrogen at high temperature and higher pressures is likely to vary. Such measurements need to be extended to higher pressures.

HISTORY OF HYDROGEN IN EARTH'S INTERIOR

D/H Constraints on the History of Deep-Seated Water

In concept, the D/H ratio (per mil δD values) of hydrogen in different reservoirs could yield first-order constraints on the likely sources of deep-Earth hydrogen, as well as provide clues to the origin of the hydrosphere. In practice, however, distinguishing between primordial and recycled water using D/H ratios is difficult,

particularly as there are fundamental uncertainties about the bulk D/H content of the planet and the rates through geologic time of mechanisms of loss of H and extraterrestrial inputs to the hydrosphere. The relative ratio of deuterium to hydrogen in mantle-derived magmas, xenoliths, and their fluid inclusions is surprisingly uniform: Relative to standard mean ocean water, the D/H ratio of such materials typically lies between −40 and −95 (e.g. Kuroda et al 1977, Boettcher & O'Neil 1980, Kyser & O'Neil 1984, Taylor & Sheppard 1986, Deloule et al 1991). These values closely reflect the isotopic composition present in the source region, as fractionation of deuterium from hydrogen at magmatic temperatures is minimal. Those magmas associated with high ("primordial") $^3He/^4He$ ratios typically lie near the lower end of this spectrum, between −80 and −85 per mil (Poreda et al 1986, Taylor & Sheppard 1986). The bulk D/H ratio of the planet is unknown, although a range of guesses for this value exist, depending on what the relative volume of mantle volatiles is assumed to be relative to the hydrosphere (e.g. Lecuyer et al 1998, Taylor & Sheppard 1986). Obviously, seawater lies at a δD value of 0, and the bulk hydrosphere (including ground water and ice) likely has a δD value of near −10 (Taylor & Sheppard 1986). However, marine sediments and subduction-associated metasediments have a range of δD values essentially identical to mantle-derived rocks (e.g. Bebout 1995). For comparison, extraterrestrial inputs have wide D/H ranges: Values between −500 and +9000 per mil have been recorded in meteorites (Yang & Epstein 1983), whereas the few constraints on the D/H ratios of comets indicate that they have heavy δD values [e.g. ∼990 per mil for comet Haley (Eberhardt et al 1995)]. Accordingly, if the cometary reservoir of water has δD values similar to that of comet Haley, then to have been derived primarily from a late cometary veneer, the hydrosphere would have had to undergo extensive isotopic fractionation. Nevertheless, δD values for carbonaceous chondrites do have an average value of near −100 (approximately $\pm$ 60) per mil (Kerridge 1985, Lecuyer et al 1998). A fundamental ambiguity in interpreting the D/H ratio of the mantle thus emerges: Marine sediments, mid-ocean ridge generated basalts, and carbonaceous chondrites each have δD ranges that strongly overlap one another. As a result, distinguishing between primordial (chondritically derived) water and water recycled into the Earth's mantle through subduction is difficult. The most parsimonious picture for the apparent contrast in the D/H content of the hydrosphere and interior involves the water currently degassed from Earth's interior being derived from an unquantified combination of primordial (chondritic) water and subduction-recycled water. In contrast, the hydrosphere's D/H ratio has likely been altered by some combination of ultraviolet-induced photochemistry (particularly for past atmospheres with larger water vapor contents), impact-induced degassing, or cometary inputs, coupled with loss of a light hydrogen component to ultimately subducted marine sediments. Each of these effects would generate preferential H-loss/D-augmentation of the proto-hydrosphere. Indeed, it is possible that the Earth's hydrosphere has steadily evolved toward heavier δD values over time from values that more precisely mimic the chondritic average (Taylor 1977, Lecuyer et al 1998).

Sources and Sinks for Water in the Earliest Earth

The evidence that hydrogen can abundantly dissolve at high pressures in iron-rich liquids and solids is irrefutable. However, whether it was incorporated in the core and how that incorporation might have occurred remains uncertain. The question of the manner and degree of hydrogen incorporation is more than casual. Virtually the entire uncertainty about the planetary complement of H stems from a lack of knowledge of how much hydrogen is sequestered in the deep Earth, particularly in the core and lower mantle. The amount of H that resides in these regions hinges on a range of accretionary and evolutionary processes. Indeed, if H is the dominant light alloying component in the Earth's core (e.g. Fukai & Suzuki 1986, Badding et al 1992), then as much as ~3% of the planet's mass is elemental hydrogen, corresponding to a planetary H content of $\sim 10^3$ times that present in Earth's hydrosphere. The enigma of the H content of Earth lies in the large cosmochemical and meteoritic abundances of hydrogen, coupled with the observation that the uppermost several hundred kilometers of the planet consist of a mantle with an average water content of only a few hundred parts per million, a variably (but still modestly) hydrated crust, and the planet's hydrosphere. The processes through which hydrogen was sequestered at depth, or lost from (or not accreted to) Earth, thus exercised a critical control on the ultimate water content of the planet. The Earth's primordial water content was governed by (*a*) the chemistry, size, and temporal distribution of accreting objects; (*b*) the efficiency with which the early planet lost water through impact-induced effects or hydrogen escape; (*c*) the efficiency of early volcanism (or magma ocean circulation) in degassing water from the interior of the planet; and (*d*) the degree (and pressures) of chemical interaction between iron-rich and hydrated material during planetary accretion and core formation.

The nature of the objects that accreted to form the Earth certainly spanned from iron-rich fragments of proto-planetary cores to largely icy cometary objects. The water content of the objects accreting to form the proto-Earth provides the first, and likely most important, step in determining the history of water on the planet. The two primary sources of water among accreting objects were likely to have been chondrites (particularly carbonaceous chondrites) and comets: Comets are probably 30%–60% water, primitive (CI-type) carbonaceous chondrites contain ~10 wt% water, and ordinary chondrites often contain ~0.2% water (e.g. see Lewis & Prinn 1984). For reference, the current hydrosphere is only ~0.02% of the mass of Earth. Therefore, the initial complement of planetary water is governed by the amount of chondrites and comets that accreted to the proto-Earth relative to achondrites and iron-rich meteorites. A discussion of the uncertainties about the water content of accreting objects is beyond the scope of this article. We simply note that the history of conjectures has varied from proposals that the planet was derived almost solely from CI chondrites to those proposing that the Earth accreted mostly from achondrites, with the hydrosphere entirely derived from a late veneer of comets or CI chondrites (Ringwood 1966, Anders 1968).

Even at present, there is considerable uncertainty about the rate of cometary input into the atmosphere/hydrosphere of the planet. These uncertainties are magnified during the early stages of accretion. The concept that a late-accreted hydrous veneer produced much of Earth's current hydrosphere has been sporadically proposed (Anders 1968, Turekian & Clark 1969, Frank et al 1986). Clearly, such an accretionary scenario implies that water presently within the planet has been regassed into the interior from near the surface: a fundamental constraint (and limit) on the degree of hydration of the planetary interior. However, as discussed above, derivation of the bulk of the hydrosphere from cometary input may be inconsistent with recent measurements of the D/H ratios of comets. For the purpose of this article, the water contents of the earlier accreting objects (on proto-planets with radii less than about 50% that of Earth) are of primary interest: These objects are not expected to be fully devolatilized by impact (e.g. Ahrens 1990) and thus are critical for emplacing water at depth within the nascent planet. As emphasized by Ringwood (1979), at least the outer portion of Earth is depleted in volatile elements relative to carbonaceous chondrites. There is a high probability that this volatilization was produced by pervasive melting and vaporization accompanying a giant (and possibly lunar forming) impact (e.g. Wetherill 1990, Cameron & Benz 1991). To what degree a giant impact could have removed water retained at depth in a proto-Earth is unclear, but simulations indicate that as much as 30% of Earth's radius could be vaporized in such an event (Cameron & Benz 1991).

The amount of water in the planet's earliest atmosphere(s) is similarly uncertain. Accretionary models have produced steam atmospheres with vapor pressures (depending on the water content of impactors) as high as >1000 bars (Abe & Matsui 1985, Zahnle et al 1988), corresponding to as many as four hydrospheres within the proto-atmosphere. The effects of such atmospheres on the chemical and thermal evolution of the early planet are huge: Through the greenhouse effect, even atmospheric water vapor contents of 20–30 bars could maintain a completely molten planetary surface (Zahnle et al 1988). Such water is, however, subject to loss through both impact erosion of the proto-atmosphere and photochemical dissociation followed by hydrogen loss. The level at which each of these loss mechanisms stripped atmospheric water from the proto-Earth is completely conjectural except that the former can apparently completely dispose of many proposed early atmospheres, with impactors of approximately lunar mass ($\sim$1% Earth mass) completely removing any extant atmosphere (Chen & Ahrens 1997, Ahrens 1993), and the latter [using Venus' essentially dry atmosphere as an illustration (Grinspoon 1993)] can likely remove at least all of the water degassed (as long as it is vaporized) from an Earth-sized body. Therefore, it is likely that any early, thick atmospheres derived from impact-induced volatile loss from (smaller) accreting objects were lost prior to their playing a role in the evolution of Earth's internal complement of water.

If the somewhat controversial premise that the early Earth was largely (and possibly completely) molten during its latter stages of accretion (Wetherill 1990, Tonks & Melosh 1993) is accurate, then the circulation pattern and depth dependence of solubility of water within a magma ocean likely controlled the degree of

degassing of the early Earth. That the solubility of water in silicate melts increases rapidly from near zero at ambient pressures to in excess of 10 wt% near 1 GPa (or 30 km depth) has long been appreciated (e.g. Burnham 1979); the solubility of water in melts at deep mantle conditions (30–42 GPa) is at least this high (e.g. Closmann & Williams 1995, Sumita & Inoue 1996). Accordingly, the solubility of water in silicate melts is effectively infinite with respect to likely water contents at mantle depths. This contrasts markedly with the solubility of water in crystalline silicate assemblages. The ability of a molten planet to retain water within its interior thus will depend on the efficiency with which magma is circulated through the uppermost ∼10 km of a terrestrial magma ocean. In this regard, the few current models of magma ocean dynamics involve probably turbulent and perhaps stratified convection within these bodies (Tonks & Melosh 1990; Solomotov & Stevenson 1993a,b; Abe 1997). It is difficult to estimate how efficiently a terrestrial magma ocean would degas, but we note that estimates of the characteristic mixing length of a convecting magma ocean are on the order of 1 km (Solomotov & Stevenson 1993a), and trapping of melt plausibly occurs near the base of the solidifying magma ocean (Tonks & Melosh 1990, Solomotov & Stevenson 1993b). Therefore, it appears that some of the water initially dissolved within a terrestrial magma ocean will likely be retained at depth in the solidifying planet. Indirect support for the existence of a hydrous magma ocean has also been derived from inferences of the pressure and temperature conditions needed to generate the siderophile trace element signature of the upper mantle during the core formation process (e.g. Righter & Drake 1999). The conditions inferred for this equilibration lie in the range of 25 GPa and 2400 K, a sufficiently low temperature that the system would have to be heavily hydrated to maintain it in a liquid state.

That some primordial water was retained at depth in Earth is also indicated by observations of ^{3}He degassing from ridges and hot spots. Because ^{3}He lacks sources sufficient to explain its currently observed degassing rate (e.g. Jambon 1994), the observation that this nonradiogenic isotope continues to be degassed implies that zones containing primordial volatiles continue to contaminate the source regions sampled by surface volcanism, and/or that the deep planet is in fact largely undegassed, with the low ^{3}He content observed simply reflecting that this deeper reservoir is (mostly) physically isolated from the shallower mantle (Kurz et al 1982, Farley et al 1992). Although providing prima facie evidence that primordial volatile material has been retained in the planet, it is important to note that the total estimated degassing rate of ^{3}He from both ridges and hot spots is about 500 mol/year, or 1.5 kg/year (Jambon 1994)—an amount so small that it serves as testimony to the efficiency with which the source region of ridges and hot spots has been degassed of its primordial helium, and perhaps to the degree of isolation of primordial volatile-bearing reservoirs as well.

As discussed above, iron and water are known to react with one another under a wide range of pressures and temperatures. As such, water-rich material will tend to oxidize metallic iron-bearing materials during accretion. The efficiency of such oxidation is not known, as it depends on the size (or surface area of contact) of iron and hydrated material, and the length of time over which they interact prior

to gravitational segregation. As such, iron-hydride forming reactions (Reaction 2 above) sequester hydrogen within Earth's core, and the pressures under which iron and hydrated material interact in the proto-Earth thus controls whether hydrogen is lost from, or buried within, the planet. Therefore, there exists an interplay between the process of core formation and the fate of water in the earliest Earth. Ideas about the process(es) by which iron segregated to the center of the planet and its degree of chemical equilibration with surrounding silicates remain controversial, but it is notable that a range of evolutionary models juxtapose relatively small iron droplets (on the order of $\sim$1 cm) with silicate melt or solid, whereas others juxtapose iron and silicates until, when the proto-planet has a size between that of Mercury and Mars, catastrophic core formation occurs (Stevenson 1990, Tonks & Melosh 1992).

Given the enormous range of uncertainties about the sources and sinks of water, what useful information can be garnered from the sketchy and speculative history of water in the Hadean? Although a surfeit of water exists in the material that accreted to form the planet, the amount that was retained (and where it was retained) remains obscure. Nevertheless, we believe that the following (by necessity unquantified, and for the most part not new) statements relevant to water in the deep planet can be made.

1. An early magma ocean could have retained significant quantities of water at depth during its solidification.
2. Primordial water exists in Earth's silicate mantle, but there is not much and/or it is not particularly accessed by the source regions of surface volcanism.
3. The current hydrosphere was (mostly) degassed from Earth's interior.
4. Some hydrogen was incorporated into the core of the planet.

Early Degassing History of the Solid Earth The issue of the rate at which the early Earth might have degassed is of seminal importance not only for the development of the hydrosphere but also for how the dynamics of Earth's deep interior might have shifted over time. In particular, the coupling between the dependence on water content of the viscosity of the upper mantle and the degassing history of the planet has been examined using parameterized convection models (McGovern & Schubert 1989, Franck & Bounama 1995). In effect, much as a temperature-dependent viscosity can regulate mantle temperatures, with the rate of temperature change of the mantle and heat flow decreasing as viscosity increases, volatile presence in the mantle can produce more rapid flow and, thus, more rapid degassing and cooling. The convective models of Earth's degassing incorporate a number of assumptions, which include the following: (*a*) that the flow laws for wet olivine rock apply throughout the mantle; (*b*) that the entire mantle is cycled through the subridge environment; and (*c*) that degassing occurs primarily at mid-ocean ridges, with essentially complete degassing of water from the uppermost 100 km of mantle in the subridge environment taking place into the basaltic oceanic crust

or hydrosphere. Although the first two of these assumptions are likely to be inaccurate, the parameterized convection models do show rapid degassing of the planet within the first 500 million years of Earth's history, with between 25% and 45% of the mantle's initial complement of water being degassed in this time period. Notably, after the first 600 million to 2 billion years of Earth's history, the regassing of the planet through subduction closely balances the degassing through mid-ocean ridge volcanism. Nevertheless, in spite of their considerable uncertainties, these models produce three useful predictions: (*a*) that considerable quantities of water are retained in the mantle (on the order of 60% of the original mantle complement, or 1.5 ocean masses of water); (*b*) that the size of the hydrosphere may have remained relatively constant from the Archean to the present; and (*c*) that much of the hydrosphere was degassed in the first several hundred million years of Earth's history.

Water Cycling During the Archean

The nature of water cycling between Earth's hydrosphere and deep interior during the Archean is considerably better understood than during the Hadean. The Archean period was likely characterized by rapid growth of continental crust and, hence, cycling of water into the interior via subduction (e.g. Campbell & Taylor 1983). In particular, the many occurrences of calc-alkaline suites in Archean terranes directly indicate the presence of hydrous melting at depth. However, the rates and efficiency with which water was cycled into, or degassed from, the Earth's interior during the Archean remain unknown: a lack of knowledge that extends to the present-day water budget. Higher radiogenic heat flow in the Archean has been used as an indication that smaller plates (and thus, more plate boundaries) existed in the Archean (Kroner 1981). This would tend to favor a larger degree of volatile recycling in this era of Earth history and consequent rapid continental crust generation. However, the rate of hydrothermal alteration of Archean oceanic crust (and, indeed, even whether ridges were entirely submerged, and whether the crust was basaltic or komatiitic) is poorly known: Indeed, little can be said beyond noting that hydrothermal systems existed in the Archean (e.g. DeRonde et al 1997).

That recycling of water from the surface into the interior took place in the Archean is clear: The degree to which the Earth's mantle had degassed at this juncture is a matter of speculation. Nevertheless, the recent idea that komatiites, highly magnesian, ultramafic rocks found almost exclusively in Archean terranes, could be generated by high-temperature hydrous melting of the Archean mantle provides a possible indication that the early mantle could have had (at least locally) high water contents (Stone et al 1997, Parman et al 1997, Asahara et al 1998, Inoue et al 2000). The magmatic water contents of the well-known Archean Barberton and Abitibi komatiites, as inferred from pyroxene compositions and the presence of primary igneous amphiboles, are startlingly high: 1%–6 wt%, with eruptive temperatures near 1400°C (Stone et al 1997, Parman et al 1997). Given the degree of partial melting of komatiites, these magmatic water contents imply that

the source region of these magmas contained ~0.5%–3% water, amounts far in excess of that associated with even subduction-related basalts today. Indeed, as noted by Parman et al (1997), a possible hydrous origin of komatiites may imply that the water content of the mantle was significantly higher and that dewatering of the planet was an ongoing phenomenon during the Archean; alternatively, locally wet, hot, possibly subduction-related environments could have existed within the Archean mantle. If correct, a hydrous origin of komatiites implies one certainty: Reasonably normal, peridotitic mantle was exposed to high water contents during the Archean; the spatial scale and precise mechanism (whether as recycled water or as primordial water) by which this exposure to water occurred remains obscure. As such, one of the prototypical Archean rock types may be a direct consequence of the presence of water at depth within the planet.

CONCLUSIONS

What the amount and processes are through which hydrogen is incorporated within Earth's interior remain remarkably uncertain. Nevertheless, some observations do imply constraints on the processes by which hydrogen was introduced into, and is sequestered within, Earth. Subduction-related material, mantle-derived hydrogen, and carbonaceous chondritic meteorites each have D/H ratios that strongly overlap, implying that the bulk of Earth's water may have been largely derived from chondritic sources and may have been incorporated within the planet during accretion. Significant cometary input of water to the planet is not directly compatible with the observed D/H ratios. The early water content of the planet likely hinged on how water was retained within an early magma ocean, and the degree to which accreted water reacted with core material.

There are indications that the upper mantle could have been significantly hydrated in the early Earth: Komatiites, an early abundant deeply-derived ultramafic magma type, may have been produced through hydrous melting of the mantle. This is in marked contrast to current-day oceanic upper mantle, which appears largely degassed: On the order of 125 ppm of water is present in the normal mid-ocean ridge basalt source region. However, more geochemically enriched (and likely more deeply derived) hot spot–associated upwelling zones have significantly higher water contents, implying that the degree of hydration of the mantle may (grossly) increase with depth. Indeed, the degree to which the lower mantle retains water depends heavily on how efficiently lower mantle material has been cycled through the upper mantle over the course of Earth's history. Yet the abundance of primordial (undegassed) water relative to recycled subducted water within the mantle remains unknown.

From a materials viewpoint, there are ample mineralogic means by which the deep Earth could retain comparatively large quantities of hydrogen. Within the shallow oceanic upper mantle, hydrogen is most likely sequestered at the 100-ppm level within nominally anhydrous phases, with possible subsidiary amphibole or mica. The subcontinental lithospheric mantle is likely more hydrated and certainly

contains amphibole or mica at shallow depths: The hydrogen abundance in subcontinental mantle at deeper depths is unknown. Through subduction, hydrogen can be retransported into the deep Earth via a variety of hydrous phases, including a range of phases normally associated with high pressure metamorphic environments. Ultimately, dense hydrous magnesium silicate phases may exist in the deep transition zone and upper portion of the lower mantle. Most hydrous phases of the deep upper mantle and transition zone are likely confined to cold subduction-related regions: only phase D, possibly members of the B-family of phases (particularly if partially fluorinated), and perhaps phase E are stable under normal mantle geotherm conditions. Hydrated, neutrally buoyant partial melts could also be present within the mantle and may represent an important water reservoir: There are seismic indications of such partially molten zones in several regions of the deep upper mantle. With the possible exceptions of β- and γ-$(Mg,Fe)_2SiO_4$, nominally anhydrous phases are unlikely to contribute more than $\sim$1 hydrosphere (and perhaps much less) to the water content of the planet: The importance of such hydration lies rather in its dramatic effect on rheology and transport properties.

The largest reservoir of hydrogen on the planet potentially lies in the core. Unfortunately, it is also the least well-understood reservoir on the planet. The amount of hydrogen incorporated into the core hinges on the degree of interaction between iron-rich material and hydrated silicates at pressures above $\sim$5 GPa during accretion and planetary differentiation. This oxygen-fugacity–dependent interaction could be better understood through a combination of improved experimental constraints and geodynamic modeling of the core formation process. The rationale for such studies is simple: The core's hydrogen content is of crucial importance for the bulk hydrogen budget of the planet, as the equivalent of up to 10^2 hydrospheres of hydrogen could be sequestered within the iron alloy of the innermost layers of the planet.

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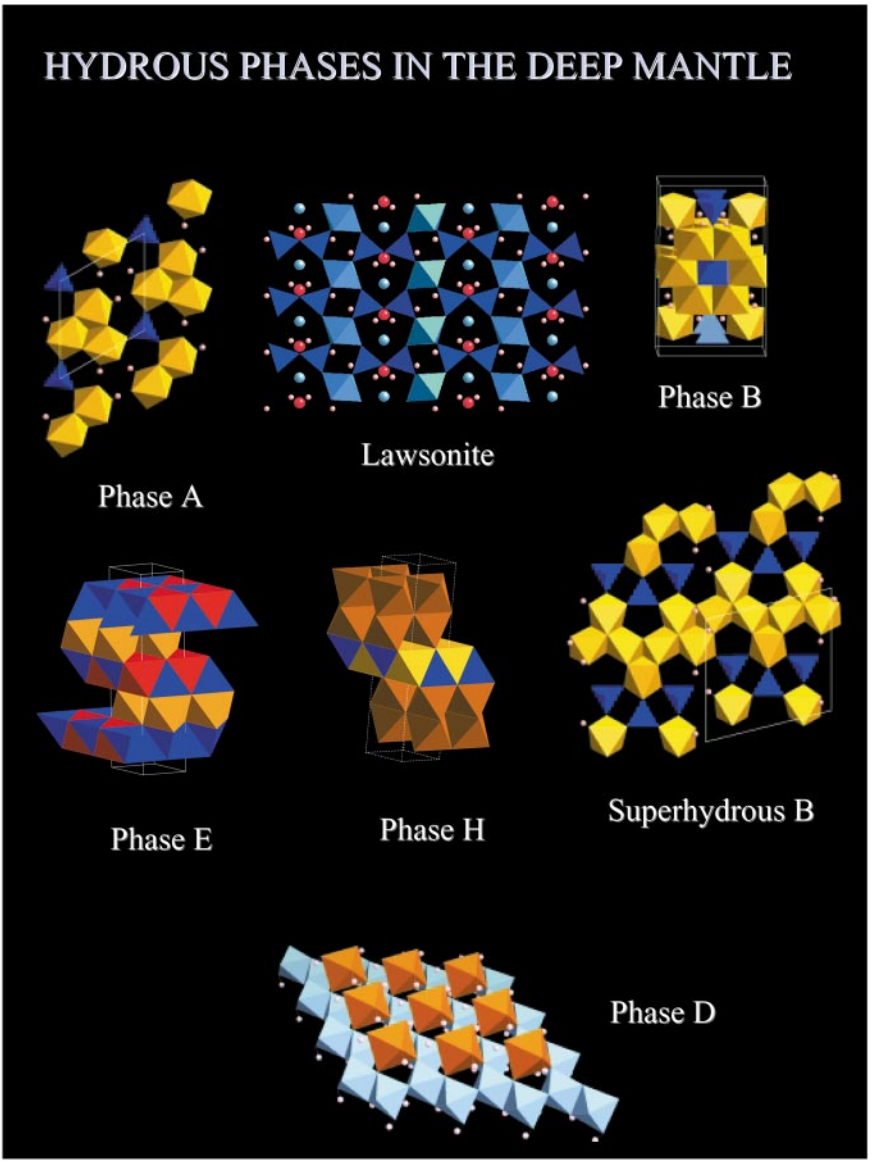

Figure 4 Crystal structures of prototype candidate hydrous phases within Earth's mantle. Structure of phase A is from Horiuchi et al (1979); lawsonite from Baur (1978); phase B from Finger et al (1991); superhydrous B is from Pacalo & Parise (1992); phase D from Yang et al (1997); phase E from Kudoh et al (1993); and phase H from Prewitt & Yang (to be published). Where their positions are known, hydrogen atom locations are shown by the small pink spheres. Calcium atoms and the oxygen of the water molecules in lawsonite are shown as blue and red spheres, respectively.

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