Water in the Mantle

Eiji Ohtani [1]

Subducting slabs transport water stored in hydrous minerals into the transition zone and lower mantle. The water storage capacity of the upper and lower mantles is less than 0.2 wt%. The transition zone has a storage capacity of approximately 0.5–1 wt% due to a water solubility of about 1–3 wt% in wadsleyite and ringwoodite, which are the major constituents of the transition zone. Thus, the transition zone may be a major water reservoir in the Earth's interior. Recent geophysical observations suggest the existence of the hydrated transition zone beneath subduction zones. Water or hydrogen may be transported as far as the bottom of the lower mantle by reacting with metallic iron in the lower mantle to form hydrous phases or iron hydride.

KEYWORDS: water, subduction, slab, mantle, transition zone, DHMS phase

INTRODUCTION

Water transport from the surface to Earth's deep interior and its circulation on a global scale are key to understanding the evolution of the planet. Peacock (1990) estimated that the amount of water transported by subducting slabs containing pelagic sediments is approximately 0.7×10^{11} kg/year for the sediments plus 8×10^{11} kg/year for the oceanic crust. Thus, the total amount of water that is returned to the Earth's mantle is estimated to be 8.7×10^{11} kg/year. This quantity is probably a lower limit, because the amount of water stored in the peridotite layer of the slabs is not included in the estimate. Peacock (1990) also estimated that the amounts of water out-gassed from the mantle through magmatism in arcs and in mid-oceanic ridges are 1.4×10^{11} kg/year and 0.6×10^{11} kg/year, respectively, giving a total amount of water out-gassed from the mantle to the surface equal to 2.0×10^{11} kg/year. This imbalance between the amount of water returned by subduction and that out-gassed from the mantle suggests that some water may be transported into the deep mantle by deep, global water circulation. Other possibilities to account for the lost water include hydration of the mantle wedge overlying the subducting slab (Peacock 1990).

Williams and Hemley (2001) discussed the global water budget and circulation (**FIG. 1**). Recent seismic tomography studies indicate that subducting slabs penetrate into the lower mantle and possibly accumulate at the mantle-core boundary (e.g., Fukao et al. 2001; Grand 2002). These observations suggest that water trapped in the slabs may be transported to the core-mantle boundary region at approximately 2900 km depth. The water transport capacity of different slabs will probably vary, depending on their thermal state. Hot and young slabs generally transport little water into the deep mantle. Colder slabs, with a lower geothermal gradient, may transport significant amounts of water into the deep mantle, although their water transport capacity is still a matter of debate (Poli and Schmidt 2002).

Water plays an important role in the evolution of Earth because water or hydrogen change the physical properties of mantle materials, including the melting temperature, viscosity, and diffusion rate. Hot plumes under wet conditions may be partially molten due to the depression of the melting temperature (e.g., Litasov and Ohtani 2003b; Ohtani et al. 2004). Water also affects mantle convection and the dynamics of ascending plumes, because a trace amount of water lowers the viscosity of the mantle through a process known as hydrolytic weakening (e.g., Mei and Kohlstedt 2000). Water also enhances the diffusion of elements and the kinetics of phase transformations (e.g., the α–β transformation in Mg_2SiO_4; Kubo et al. 1998). Water affects the position of phase boundaries such as the α–β transformation in the Mg_2SiO_4–Fe_2SiO_4 system (e.g., Wood 1995) and is responsible for the transport of dissolved components.

In this paper, we review the mechanisms of water transport into the transition zone and lower mantle by subducting slabs and the water storage capacity of the mantle. We also present evidence for the existence of water in subducting slabs, at the base of the upper mantle, and in the transition zone.

TRANSPORT OF WATER IN THE MANTLE

A number of studies have clarified the stability of hydrous phases in peridotite, basalt, and sediment components of slabs at high pressure and temperature. Ringwood and his colleagues made pioneering studies of the existence and stability of hydrous minerals and reported several high-pressure hydrous mineral phases such as phases A, B, and C (e.g., Ringwood and Major 1967). These mineral phases are dense hydrous magnesium silicates, DHMS (**TABLE 1**). Many hydrous mineral phases, including DHMS, are stable only at the low temperatures representative of slab conditions; they are not stable along the normal mantle geotherm.
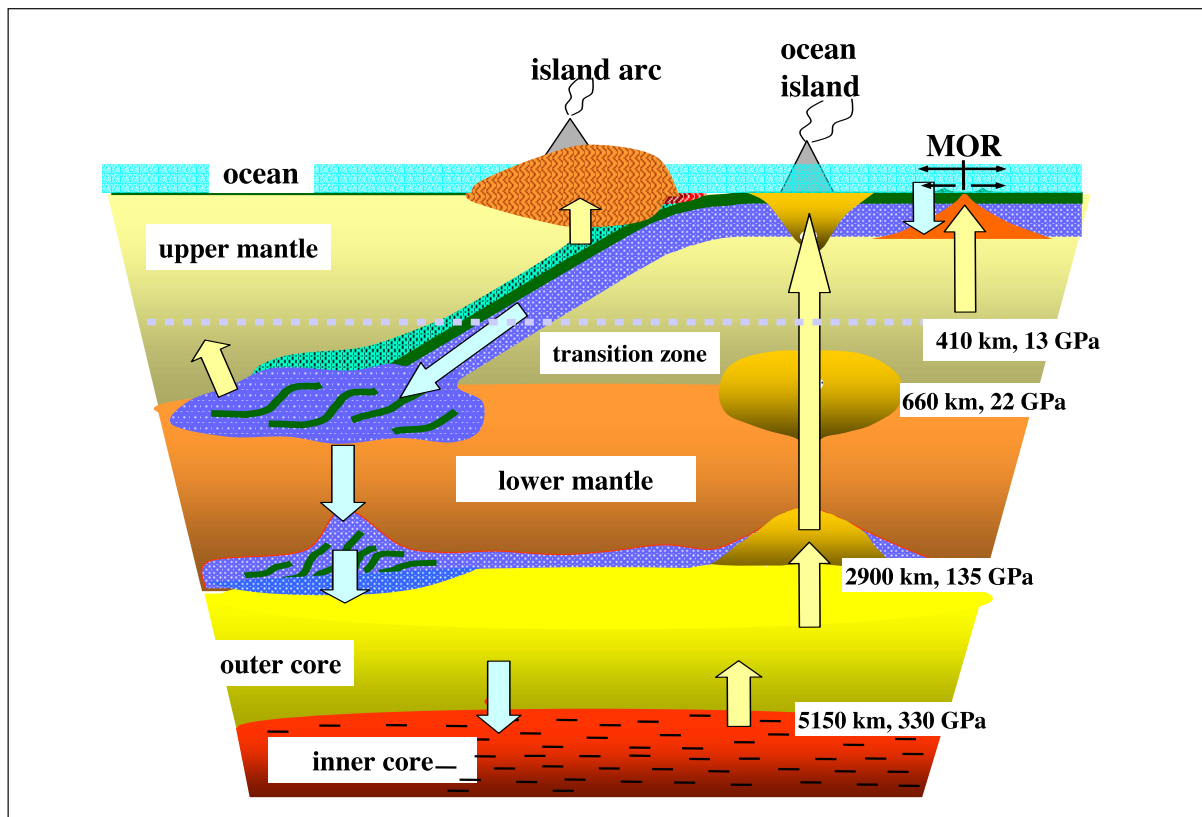
In the peridotite layer of subducting slabs, a series of hydrous phases are stable along the slab geotherm (**FIG. 2**). The major hydrous phases in the peridotite layer of the slab change continuously from chlorite to serpentine to the 10Å phase (Fumagalli et al. 2001) in the upper mantle. At higher pressures, water can be transported by phase A, the stability of which overlaps that of serpentine or the 10Å phase in cold slabs (e.g., Poli and Schmidt 2002). Water can also be transported by phase E, wadsleyite, and ringwoodite. The major phases in the transition zone, wadsleyite and ringwoodite, can accommodate 1 to 3 wt% water as shown in **TABLE 1** (e.g., Inoue et al. 1995; Kohlstedt et al. 1996). Superhydrous phase B (which is identical to phase C) can also serve as a water reservoir at the base of the transition zone depending on the water content in the slab. This phase is formed by decomposition of hydrous ringwoodite at the base of the transition zone (Fig. 2). Superhydrous phase B is stable to the top of the lower mantle at a pressure of approximately 30 GPa. It decomposes into periclase, Mg-perovskite, and phase D (identical to phase G), another important hydrous phase that is stable to a pressure of 45 GPa (Shieh et al. 1998).

Extensive work has been conducted on the metamorphic phase relations of the basalt-water system up to 2.5 GPa (e.g., Thompson et al. 1982). Hydrous phases such as lawsonite, zoisite, and chlorite are stable in the hydrated basalt system under these conditions (e.g., Poli and Schmidt 1995). Lawsonite, usually observed in the blueschist facies, has an extremely wide stability field and may occur at pressures as high as 10 GPa or more, which corresponds to a depth of 300 km in the subduction zone environment. Because lawsonite contains a large amount of water (up to 11.5 wt%) and has a wide stability field, it could be a primary carrier of water into the transition zone. Although no hydrous phases exist in the basalt-water system at higher pressures (Okamoto and Maruyama 2004), water (in the form of hydrous phases) trapped in the overlying sediments

or in the peridotite mantle wedge adjacent to the slab can be transported farther into the lower mantle (e.g., Ono 1998; Schmidt and Poli 1998).

Hydrous phases present in pelagic sediments can be estimated based on phase relations in the Al_2O_3–SiO_2–H_2O system. Diaspore (AlOOH) and phase Π [$Al_3Si_2O_7(OH)_3$] are stable to pressures of 6 GPa, and these phases react with
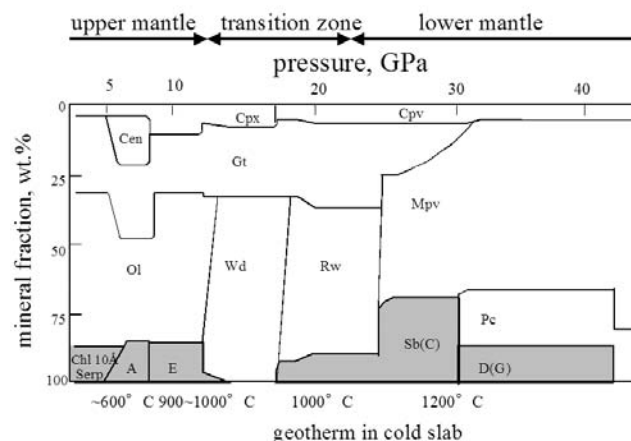
SiO$_2$ to form hydrous topaz [Al$_2$SiO$_4$(OH)$_2$; Wunder et al. 1993a, b], which is stable up to 11 GPa at 1000°C. At higher pressures, topaz-OH reacts with SiO$_2$ to form phase Egg [AlSiO$_3$OH; Eggelton et al. 1979; Schmidt et al. 1998; Ono 1999]. Phase Egg decomposes to stishovite and the hydrous phase δ–AlOOH, which is the high-pressure polymorph of diaspore at the top of the lower mantle along the cold slab geotherm (Sano et al. 2004). Phase Egg is stable to temperatures above 1400°C at transition zone depth and decomposes into corundum + stishovite + fluid at higher temperatures (**FIG. 3A**). In the basalt–water system, no hydrous phase exists after the decomposition of lawsonite in the transition zone, and the fluid formed by dehydration of lawsonite is likely contained in phase Egg or phase δ–AlOOH in the overlying sediment component of the slab.

Name	Formula*	Density g/cm^3	Mg/Si	H$_2$O wt.%
chlorite	Mg$_5$Al$_2$Si$_3$O$_{10}$(OH)$_8$	2.6-3.4	1.67	13
serpentine	Mg$_3$Si$_2$O$_5$(OH)$_4$	2.55	1.5	14
chondrodite	Mg$_5$Si$_2$O$_8$(OH)$_2$	3.06-3.16	2.5	5.3
hydroxylclinohumite	Mg$_9$Si$_4$O$_{16}$(OH)$_2$	3.14-3.26	2.25	3
10Å phase	Mg$_3$Si$_4$O$_{14}$H$_6$	2.65	0.75	13
phase A	Mg$_7$Si$_2$O$_8$(OH)$_6$	2.96	3.5	12
phase B	Mg$_{12}$Si$_4$O$_{19}$(OH)$_2$	3.38	3	2.4
superhydrous phase B(= phase C)	Mg$_{10}$Si$_3$O$_{14}$(OH)$_4$	3.327	3.3	5.8
phase D(= phase F =phase G)	Mg$_{1.14}$Si$_{1.73}$H$_{2.81}$O$_6$	3.5	0.66	14.5~18
phase E	Mg$_{2.3}$Si$_{1.25}$H$_{2.4}$O$_6$	2.88	1.84	11.4
wadsleyite	Mg$_2$SiO$_4$	3.47	2	≤3
ringwoodite	Mg$_2$SiO$_4$	3.47-3.65	2	1.0-2.2
topaz-OH	Al$_2$SiO$_4$(OH)$_2$	3.37	-	10
diaspore	AlOOH	2.38	-	15
phase Π	Al$_3$Si$_2$O$_7$(OH)$_3$	3.23	-	9
phase EGG	AlSiO$_3$OH	3.84	-	7.5
phase δ	AlOOH	3.533	-	15
lawsonite	CaAl$_2$Si$_2$O$_{10}$H$_4$	3.09	-	11.5

* End-member formulas

STORAGE OF WATER IN EARTH'S INTERIOR

Water transported into the mantle must be stored mainly in nominally anhydrous minerals, as most of the hydrous phases are not stable along the normal mantle geotherm. The solubility of water in nominally anhydrous minerals has been measured for phases that occur under mantle conditions (e.g., Bolfan-Casanova et al. 2000). The water content of lower mantle minerals such as Mg-perovskite, Ca-perovskite, and magnesiowüstite are summarized in **TABLE 2**. Note that the maximum water

solubility varies with the composition of the Mg-perovskite phases. Pure MgSiO$_3$ perovskite contains less than 500 ppm water (e.g., Meade et al. 1994; Bolfan-Casanova et al. 2002; Litasov et al. 2003), and aluminous perovskite (Al–Mg-perovskite or Al–Fe–Mg-perovskite) in mantle peridotite contains 1100–1800 ppm water. On the other hand, Al–Fe–Mg-perovskite in the basaltic component of the slab contains only 100–400 ppm water (Litasov et al. 2003)

The average lower mantle consists of 80 wt% Mg-perovskite, 15 wt% magnesiowüstite, and 5 wt% Ca-perovskite. Ca-perovskite and magnesiowüstite can accommodate about 0.3–0.4 wt% and 0.2 wt% water, respectively (Murakami et al. 2002). However, Bolfan-Casanova et al. (2002) and Litasov et al. (2003) both reported water contents for magnesiowüstite that are lower than those reported by

Mineral phases	SiO$_2$	TiO$_2$	Al$_2$O$_3$	FeO§	MgO	Mg#	Pressure GPa	Temperature °C	H$_2$O ppmwt	1σ	References
MgSiO$_3$ perovskite	60.1				40.36	100	25	1300	104	14	1)
Al-Mg perovskite	59.09		2.03		39.77	100	25	1400	101	19	1)
Al-Mg perovskite	57.86		4.43		39.55	100	25	1200	1101	156	1)
Al-Mg perovskite	55.37		7.16		38.18	100	26	1200	1440	160	1)
Al-Fe-Mg perovskite*	36.73	2.18	14.5	26.23	20.15	57.8	26	1000	110	21	1)
Al-Fe-Mg perovskite*	38.11	1.91	13.16	24.52	21.37	60.8	26	1200	104	26	1)
Al-Fe-Mg perovskite*	38.43		16.77	23.4	20.82	61.3	25	1300	47	12	1)
Al-Fe-Mg perovskite**	52.77		5.5	7.39	34.48	0.18	25	1400	1780	175	1)
Al-Fe-Mg perovskite**	53.11		5.8	6.09	34.94	0.15	25	1600	1460	130	1)
MgSiO$_3$ perovskite	60.1				40.36	100	27	1500	60-70		2)
MgSiO$_3$ perovskite	60.1				40.36	100	24	1600	<1		3)
Al-Fe-Mg perovskite**			2~6	1~4		100	24		<5		3)
Al-Fe-Mg perovskite**							25.5		1000~4000		4)
Magnesiowüstite (=Ferropericlase)							25.5		2000		4)
Periclase					100	100	24	1600	2		3)
CaSiO$_3$ perovskite							25.5		3000-4000		4)

All "perovskites" in table = silicates with a perovskite-like structure. *: in MORB; **: in peridotite; 1) Litasov et al. (2003); 2) Meade et al. (1994); 3) Bolfan-Casanova et al. (2000); 4) Murakami et al. (2001); §: Iron calculated as ferrous iron

Murakami et al. (2002). From the results on water solubility in lower mantle minerals, we estimate that the average lower mantle peridotite can contain 0.15 to 0.2 wt% water. Therefore, the water storage potential of the lower mantle is estimated to be 3.4–4.5 × 10^{21} kg. This is about 2.5–3 times the present ocean mass and is comparable to the amount of water stored in the transition zone.

The major minerals in the transition zone, wadsleyite and ringwoodite, can accommodate a large amount of water. Litasov and Ohtani (2003a) have shown that the maximum water content of wadsleyite at 15 GPa decreases with increasing temperature from 2 wt% at 1000°C to 0.5 wt% at 1600°C, and it decreases further to 0.3 wt% at 18 GPa and 1600°C. Thus, the shallower transition zone has a larger storage capacity for water than the deeper transition zone. The water content of ringwoodite also decreases with increasing temperature at 20 GPa from 2 wt% at 1000°C to 0.5 wt% at 1600°C, although it has a weaker pressure dependence as compared with wadsleyite (Ohtani et al. 2000; Litasov and Ohtani 2003a). The maximum water storage capacity of wadsleyite and ringwoodite is estimated to be about 0.5–1 wt% along the normal mantle geotherm, which corresponds to an amount of water in the mantle two to three times that of the present ocean mass.

Although there are some uncertainties in the water storage capacity of lower mantle minerals, we can generally conclude that there is a layered structure in the water storage capacity of the mantle. The upper and lower mantles have relatively low water storage capacities, whereas the transition zone has a higher water storage capacity. A relatively low water storage capacity in the lower mantle indicates that slabs being subducted into the lower mantle dehydrate at the top of the lower mantle. The water content of the transition zone might be large because the dehydrated water from the subducted slabs together with primordial water in the lower mantle are stored in the transition zone over geologic time.

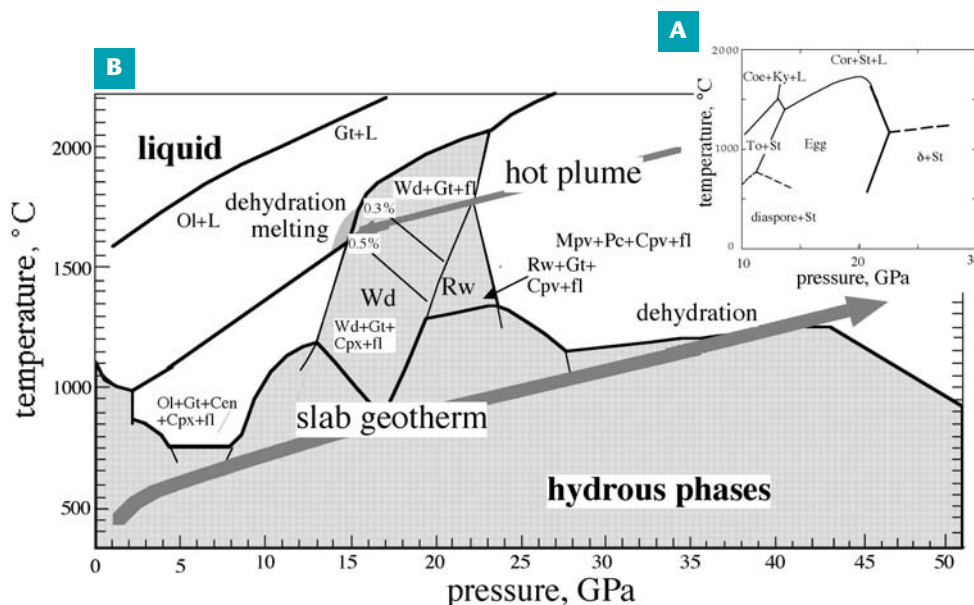## GEOPHYSICAL EVIDENCE FOR WATER IN THE DEEP MANTLE

Superhydrous phase B decomposes to Mg-perovskite, periclase, and fluid at 30 GPa and above 1200°C; however, it decomposes into hydrous phase D, Mg-perovskite, and periclase at the same pressure below 1200°C (Ohtani et al. 2003). Water stored in ringwoodite and superhydrous phase B in the transition zone and the uppermost lower mantle may dehydrate at the top of the lower mantle in stagnant slabs (**FIG. 3B**). Thus, the uppermost lower mantle may be one of the major dehydration regions in the mantle.

In a cold slab, water may be transported into the lower mantle by hydrous phase D (= phase G), which is stable up to about 40 GPa or a depth of 1200 km. At greater pressure, the hydrous phase breaks down (Shieh et al. 1998). Thus, dehydration of a subducting slab could occur in four different regions depending on the temperature profiles of the slabs: (1) the uppermost mantle by the decomposition of serpentine, chlorite, phengite, and lawsonite, which could trigger island arc volcanism; (2) the transition zone by decomposition of phase E and the decrease in the solubility of water in wadsleyite with increasing depth; (3) the upper part of the lower mantle by decomposition of hydrous ringwoodite and/or the superhydrous phase B; and (4) the deep lower mantle (~1200 km) by the decomposition of phase D in the slab (Shieh et al. 1998). Additionally, the base of the upper mantle could be a region of dehydration melting of rising hot and wet plumes, as shown in Figure 3b.

A melt may exist at the base of the upper mantle or above the 410-km discontinuity beneath eastern China (Revenaugh and Sipkin 1994). P-wave tomography studies of those zones and beneath Japan (Zhao 2001, 2004; Fukao et al. 2001) suggest the existence of low-velocity anomalies at the base of the upper mantle and the top of the lower mantle. These sites, as well as the top and base of the transition zone, are plausible sites for dehydration and/or dehydration melting (Fig. 3b).
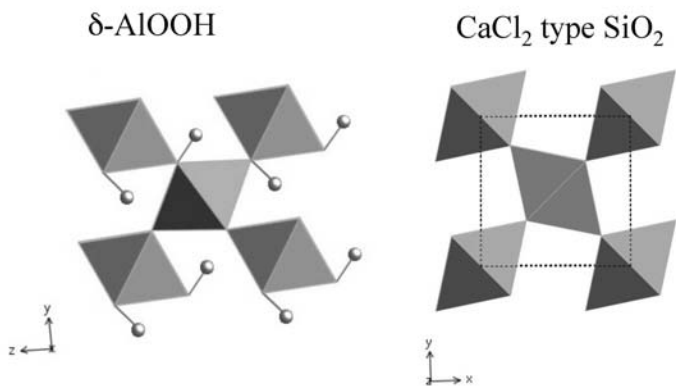
A large (60–70 km) upward deflection of the 410-km discontinuity in the Izu–Bonin slab has been reported by Collier et al. (2001). They have argued that the discontinuity can be explained by the equilibrium olivine–wadsleyite transformation boundary in the cold slab. Such a large elevation of the 410-km discontinuity corresponds to a slab that is 500°C cooler than the surrounding normal mantle. In such a cold slab condition, metastable olivine is inevitable due to its sluggish transformation kinetics under dry conditions (e.g., Rubie and Ross 1994), and a depression of the 410-km discontinuity is expected in cold slabs due to the metastability of dry olivine. The elevation of the 410-km discontinuity may reflect the wet condition of the slab, as a small amount of water (0.12–0.5 wt%) speeds up the olivine-to-wadsleyite phase transformation and is equivalent to a temperature increase of 150°C. Thus, the location of the 410-km discontinuity in the cold Izu–Bonin slab can be explained as the elevation of the olivine–wadsleyite equilibrium phase boundary due to wet conditions. Additionally, seismologi-

δ-AlOOH   CaCl₂ type SiO₂

FIGURE 4 Structure of δ–AlOOH (Suzuki et al. 2000; Tsuchiya et al. 2002) and CaCl₂-type SiO₂. Aluminum and silicon atoms are at the center of the octahedron of oxygen atoms in δ–AlOOH and CaCl₂-type SiO₂, respectively. Small circles in the δ–AlOOH structure are hydrogen atoms.

FIGURE 5 The process in the slabs subducting into the lower mantle. Water can be generated by dehydration from decomposition of superhydrous phase B and phase D. Metallic iron can be generated associated with the garnet-perovskite transformation (Miyajima et al. 1999; Frost et al. 2004). Metallic iron and water react to form iron oxide and iron hydride in the lower mantle. The model provides a possible mechanism of hydrogen transport into the base of lower mantle.

cal evidence for depression of the 410-km discontinuity originating from the metastable olivine core is not observed in the Tonga slab (Koper et al., 1998). Thus, current seismic observations of the depth of the 410-km discontinuity may be consistent with a wet slab descending into the transition zone. However, this conclusion is not definitive. Dry kinetics determined experimentally might not be applicable to the long time-scales, stress regime, or grain size within slabs.

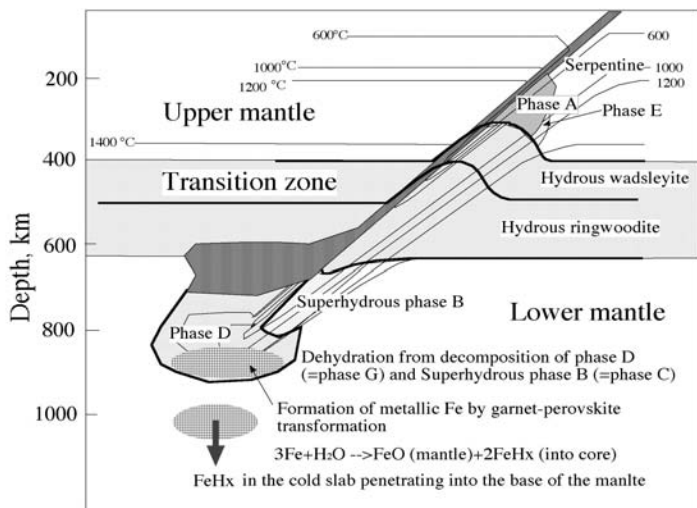## WATER TRANSPORT INTO THE LOWER MANTLE AND CORE MANTLE BOUNDARY

Water can be transported into the lower mantle by hydrous phases, such as superhydrous phase B, phase D, phase Egg, and phase δ. However, these phases probably decompose and dehydrate at the pressure and temperature conditions of the deep lower mantle, although the stability limit of phase δ–AlOOH has not yet been confirmed. Thus, most of the water stored in hydrous minerals in subducting slabs is removed from the slabs by dehydration.

The δ–AlOOH phase is a potential phase to transport water into the deeper lower mantle. This phase has a structure similar to post-stishovite SiO₂ with a CaCl₂ structure (see **FIG. 4**), and it forms over a wide range of compositions in the solid solution between AlOOH and $Mg_{0.5}Si_{0.5}OH$ (Suzuki et al. 2000; Tsuchiya et al. 2002). This phase has a bulk modulus of about 250 GPa, comparable to corundum Al_2O_3, which has the highest bulk modulus of any hydrous phase ever synthesized, even though it contains a large amount of water (Vanpeteghem et al. 2002). Therefore, it could be a candidate to transport water into the deep lower mantle, although its stability in the descending slab and the lower mantle peridotite is not yet clear.

Water may be transported by other mechanisms. A small amount of metallic iron (about 1 wt%) may be present in the lower mantle (Miyajima et al. 1999; Frost et al. 2004). Metallic iron can be formed by transformation of garnet to aluminous perovskite, which contains a large amount of ferric iron (e.g., McCammon 1997; Litasov et al. 2003). Thus, metallic iron may react with water dehydrated from a slab according to the reaction: $3Fe+H_2O \rightarrow 2FeH_x+FeO$. A schematic model of the reaction of metallic iron and water at the top of the lower mantle is shown in **FIG. 5**. The phase relations of this reaction have been thermodynamically analyzed by Badding et al. (1992) and experimentally investigated by Saxena et al. (2004) and Ohtani et al. (2005). The reaction occurs at pressures above 6 GPa and temperatures above 700°C. Thus, FeH_x can be formed in slabs descending into the lower mantle when metallic iron and water are generated at the top of the lower mantle. FeO formed by this reaction can further react to form magnesiowüstite in the lower mantle. Several polymorphs of FeH_x have been reported. Under water-saturated conditions, a double hexagonal phase (dhcp FeH_x, x~1.0) is stable at pressures above 5 GPa and temperatures below 900°C, whereas a γ–FeH_x phase (x~1) is stable above 900°C. When the system is not saturated with water, hydrogen can be stored in the interstices of ε–Fe (hcp iron) structure. Thus, FeH_x phases may be candidates for the transport of hydrogen to the base of the lower mantle.

ACKNOWLEDGMENTS

REFERENCES

Badding JV, Mao HK, Hemley RJ (1992) High-pressure crystal structure and equation of state of iron hydrate: implications for the Earth's core. In: Syono Y and Manghnani MH (eds) High-pressure research: application to Earth and planetary Sciences, Terabub, Japan, and AGU, Washington, DC, pp 353-371

Bolfan-Casanova N, Keppler H, Rubie DC (2000) Water partitioning between nominally anhydrous minerals in the $MgO–SiO_2–H_2O$ system up to 24 GPa: implications for the distribution of water in the Earth's mantle. Earth and Planetary and Science Letters 182: 209–221

Bolfan-Casanova N, Mackwell S, Keppler H, McCammon C, Rubie DC (2002) Pressure dependence of H solubility in magnesiowüstite up to 25 GPa: Implications for the storage of water in the Earth's lower mantle. Geophysical Research Letters 29(10): 1449, doi: 10.129/2001 GL014457

Collier JD, Helffrich GR, Wood BJ (2001) Seismic discontinuities and subduction zones. Physics of the Earth and Planetary Interiors 127: 35–49

Eggelton RA, Boland NJ, Ringwood A (1979) High pressure synthesis of a new aluminum silicate: $Al_5Si_5O_{17}(OH)$. Geochemical Journal 12: 191-194

Frost DJ, Liebske C, Langenhorst F, McCammon C, Tronnes RG, Rubie DC (2004) Experimental evidence of iron-rich metal in the Earth's lower mantle. Nature 428: 409-411

Fukao Y, Widiyantoro S, Obayashi M (2001) Stagnant slabs in the upper and lower mantle transition region. Review of Geophysics 39: 291-323

Fumagalli P, Stixrude L, Poli S, Snyder D (2001) The 10Å phase: a high-pressure expandable sheet silicate during subduction of hydrated lithosphere. Earth and Planetary Science Letters 186: 125–141

Grand SP (2002) Mantle shear-wave tomography and the fate of subducted slabs. Philosophical Transactions of the Royal Society of London A 360: 2475-2491

Inoue T, Yurimoto H, Kudoh Y, (1995) Hydrous modified spinel, $Mg_{1.75}SiH_{0.5}O_4$: A new water reservoir in the mantle transition region. Geophysical Research Letters 22(2): 117-120

Kohlstedt DL, Keppler H, Rubie DC (1996) Solubility of water in the α, β, γ phases of $(Mg,Fe)_2SiO_4$. Contributions to Mineralogy and Petrology 123: 345-357

Koper KD, Wiens DA, Dorman LM, Hildebrand JA, Webb SC (1998) Modeling the Tonga slab: Can travel time data resolve a metastable olivine wedge? Journal of Geophysical Research 103(B12): 30079–30100

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

Litasov K, Ohtani E (2003a) Stability of various hydrous phases in CMAS pyrolite–H_2O system up to 25 GPa. Physics and Chemistry of Minerals 30: 147–156

Maruyama S, Isozaki Y, Nakashima S, Windley BF (2001) History of the Earth and Life. In: Nakashima S et al. (eds) Geochemistry and the origin of life, Universal Academic Press, Tokyo, Japan, pp 285-325

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

Mei S, Kohlstedt DL (2000) Influence of water on plastic deformation of olivine aggregates 1. Diffusion creep regime. Journal of Geophysical Research 105(B9): 21457-21469

Miyajima N, Fujino K, Funamori N, Kodo T, Yagi T (1999) Garnet-perovskite transformation under conditions of the Earth's lower mantle: an analytical transmission electron microscopy study. Physics of the Earth and Planetary Interiors 116: 117-131

Murakami M, Hirose K, Yurimoto H, Nakashima S, Takafuji N (2002) Water in Earth's lower mantle. Science 295: 1885-1887

Ohtani E, Mizobata H, Yurimoto H (2000) Stability of dense hydrous magnesium silicate phases in the systems Mg_2SiO_4-H_2O and $MgSiO_3$-H_2O at pressures up to 27 GPa. Physics and Chemistry of Minerals 27: 533-544

Ohtani E, Toma M, Kubo T, Kondo T, Kikegawa T (2003) In situ X-ray observation of decomposition of superhydrous phase B at high pressure and temperature. Geophysical Research Letters 30 (2): 1029, doi: 10.1029 /2002 GL015549

Ohtani E, Litasov K, Hosoya T, Kubo T, Kondo T (2004) Water transport into the deep mantle and formation of a hydrous transition zone. Physics of the Earth and Planetary Interiors 143-144: 255-269

Ohtani E, Hirao N, Kondo T, Ito M, Kikegawa T (2005) Iron-water reaction at high pressure and temperature, and hydrogen transport into the core. Physics and Chemistry of Minerals: in press

Okamoto K, Maruyama S (2004) The eclogite-garnetite transformation in MORB+H_2O system. Physics of the Earth and Planetary Interiors 146: 283-296

Ono S (1998) Stability limits of hydrous minerals in sediment and mid-ocean ridge basalt compositions: Implications for water transport in subduction zones. Journal of Geophysical Research 103: 18253-18268

Ono S (1999) High temperature stability limit of phase egg, $AlSiO_3(OH)$. Contributions to Mineralogy and Petrology 137: 83-89

Peacock SM (1990) Fluid processes in subduction zone. Science 248: 329–337

Poli S, Schmidt MW (1995) H_2O transport and release in the transition zones–experimental constraints on basaltic and andesitic systems. Journal of Geophysical Research 100:1061-1107

Poli S, Schmidt MW (2002) Petrology of subducted slabs. Annual Review of Earth and Planetary Science 30: 207–235

Revenaugh J, Sipkin SA (1994) Seismic evidence for silicate melt atop the 410-km mantle discontinuity. Nature 369: 474-476

Ringwood AE, Major A (1967) High-pressure reconnaissance investigations in the system Mg_2SiO_4-MgO-H_2O. Earth and Planetary Science Letters 2: 130-133

Rubie DC, Ross II CR (1994) Kinetics of the olivine-spinel transformation in subducting lithosphere: experimental constraints and implications for deep slab processes. Physics of the Earth and Planetary Interiors 86: 223–241

Sano A, Ohtani E, Kubo T, Funakoshi K (2004) In situ X-ray observation of decomposition of hydrous aluminum silicate $AlSiO_3OH$ and aluminum oxide hydroxide δ-AlOOH at high pressure and temperature. Journal of Physics and Chemistry of Solids 65: 1547-1554

Saxena SK, Lierman H-P, Shen G (2004) Formation of iron hydride and high-magnetite at high pressure and temperature. Physics of the Earth and Planetary Interiors 146: 313-317

Schmidt MW, Poli S (1998) Experimentally based water budgets for dehydrating slabs and consequences for arc magma generation. Earth and Planetary Science Letters 163: 361–379

Schmidt MW, Finger LW, Angel RJ, Dinnebier RE (1998) Synthesis, crystal structure, and phase relations of $AlSiO_3(OH)$, a high-pressure hydrous phase. American Mineralogist 83: 881-888

Shieh SR, Mao HK, Hemley RJ, Ming LC (1998) Decomposition of phase D in the lower mantle and the fate of dense hydrous silicates in subducting slabs. Earth and Planetary Science Letters 159: 13-23

Suzuki A, Ohtani E, Kamada T (2000) A new hydrous phase δ-AlOOH synthesized at 21GPa and 1000°C. Physics and Chemistry of Minerals 27: 689-693

Thompson JB, Laird J, Thompson AB (1982) Reactions in amphibole, greenschist and blue schist. Journal of Petrology 23: 1-27

Tsuchiya J, Tsuchiya T, Tsuneyuki S, Yamanaka T (2002) First principles calculation of a high-pressure hydrous phase, δ-AlOOH. Geophysical Research Letters 29: doi10.1029/2002GL015417

Vanpeteghem CB, Ohtani E, Kondo T (2002) Equation of state of the hydrous phase δ-AlOOH at room temperature up to 22.5 GPa. Geophysical Research Letters 29 (7), doi: 10.1029/2001GL014224

Williams Q, Hemley RJ (2001) Hydrogen in the deep earth. Annual Review of Earth and Planetary Science 29: 365-418

Wood BJ (1995) The effect of H_2O on the 410-kilometer seismic discontinuity. Science, 268: 74-76

Wunder B, Medenbach O, Krause W, Schreier W (1993a) Synthesis, properties and stability of $Al_3Si_2O_7(OH)_3$ (phase pi) a hydrous high pressure phase in the system Al_2O_3-SiO_2-H_2O. European Journal of Mineralogy 5: 637-649

Wunder B, Rubie CD, Ross CR, Medenbach O, Seifert F, Shreier W (1993b) Synthesis, stability and properties of $Al_2SiO_4(OH)_2$: a fully hydrated analogue of topaz. American Mineralogist 78: 285-297

Zhao D (2001) Seismological structure of subduction zones and its implications for arc magmatism and dynamics. Physics of the Earth and Planetary Interiors 127: 197-214

Zhao D (2004) Global tomographic images of mantle plumes and subducting slabs: Insight into deep Earth dynamics. Physics of the Earth and Planetary Interiors 146: 3-34 ◼