The role of water in Earth’s mantle

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ABSTRACT

Geophysical observations suggest that the transition zone is wet locally. Continental and oceanic sediment components together with the basaltic and peridotitic components might be transported and accumulated in the transition zone. Low-velocity anomalies at the upper mantle–transition zone boundary might be caused by the existence of dense hydrous magmas. Water can be carried farther into the lower mantle by the slabs. The anomalous Q and shear wave regions locating at the uppermost part of the lower mantle could be caused by the existence of fluid or wet magmas in this region because of the water-solubility contrast between the minerals in the transition zone and those in the lower mantle. $\delta$-H solid solution $\text{AlO}_2\text{H}$–$\text{MgSiO}_3\text{H}_2$ carries water into the lower mantle. Hydrogen-bond symmetrization exists in high-pressure hydrous phases and thus they are stable at the high pressures of the lower mantle. Thus, the $\delta$-H solid solution in subducting slabs carries water farther into the bottom of the lower mantle. Pyrite $\text{FeO}_2\text{H}_x$ is formed due to a reaction between the core and hydrated slabs. This phase could be a candidate for the anomalous regions at the core–mantle boundary.

Keywords: water, hydrous phase, subducting slab, transition zone, lower mantle, hydrogen-bond symmetrization, core–mantle boundary

INTRODUCTION

Hydrogen is the most abundant element in the solar abundance. There are various modes of occurrence of hydrogen on Earth. Hydrogen exists as water vapor in the atmosphere, and water and ice in the ocean and land water, super-critical fluids in the volcanoes and Earth crusts, hydroxyls in hydrous and nominally anhydrous minerals in the crust and mantle, proton and hydroxyl (OH) in magmas, and hydrogen in metallic iron in the core.

Hydrogen and water play important roles in the dynamics of Earth’s interior. They lower the internal friction of rocks and cause earthquakes, and dehydration embrittlement, namely the dehydration of hydrous minerals (such as serpentine) that causes fracturing. Water generates magmas by lowering the melting temperature of silicates in the mantle. Water softens rocks, namely water weakening, and enhances mantle convection.

The flux of water on Earth has been estimated by several authors. According to Peacock [1], the amount of water degassed to the surface through magmatism is $2 \times 10^{11}$ kg/year. The water flux returned to the mantle by subducting slabs is $\sim 8.7 \times 10^{11}$ kg/year. Thus, $6.7 \times 10^{11}$ kg/year of water move to the deep interior associated with slab subduction. According to Wallace [2], there might be a balance in the flux of water between the input through subducting slabs and the output through degassing through arc volcanism to the surface, both with $3 \times 10^{11}$ kg/year. On the other hand, van Keken et al. [3] estimated that a third of water, i.e. $7–10 \times 10^{11}$ kg/year, penetrating through subduction is recycled into the mantle, whereas two-thirds of this water is degassed through dehydration of the slabs during subduction. In spite of uncertainties, it is important to specify the water reservoirs in the mantle, since a small amount of water can modify the properties of mantle materials.

The water contents were estimated by many procedures such as mineral inclusions in diamond, fluid or glass inclusions in magmas, mineral physics and the phase stability of the water-bearing system, and geophysical observations such as electrical conductivity and seismic observations. Reliable estimation of global water contents in the mantle is obtained by geophysical observations, since other procedures may represent the water contents in
local regions, and the average water content may be different due to heterogeneity in the mantle. The water contents in Earth’s interior estimated by geophysical observations are summarized in Table 1. Extensive studies have agreed that the transition zone is a major water reservoir, but the water storage in the lower mantle is poorly constrained. The water contents summarized in Table 1 indicate that the upper mantle, mantle transition zone and lower mantle contain 0.04, 0.2–1 and < 2 oceans of water, respectively. Here, we discuss the various processes related to water in the upper mantle, transition zone, lower mantle and the core–mantle boundary, such as the water distribution, hydrous minerals and their O–H bonding nature, and the effects of water in the seismic anomalies and mantle dynamics.

### ROLE OF WATER IN THE UPPER MANTLE AND THE MANTLE TRANSITION ZONE

#### Water in the upper mantle

The water content stored in the upper mantle estimated by various methods is shown in Table 1. Electrical conductivity data suggest the normal upper mantle is essentially dry and its water content is less than 100 ppm [4] or ~100 ppm [5]. The average water content in olivine, orthopyroxene and clinopyroxene in the Udachinaya peridotite xenolith has been reported as 1–64 ppm [6], although a high water content 300 ppm of olivine due to metasomatism is reported in the same xenolith [7]. The water contents in the MORB (mid-oceanic ridge basalt) and OIB (ocean island basalt) source mantles are estimated to be 0.01 and 0.075 wt.% respectively, based on the H$_2$O/Ce ratio in basalt glasses [8]. These estimations indicate that the upper mantle is not homogeneous and the normal mantle represented by the depleted mantle of the MORB source is generally dry, with ~100 ppm or less of water, whereas the OIB source mantle is wet, with water contents of ~0.075 wt.%.

On the other hand, the water content in subducting slabs descending in the upper mantle is estimated to be 1–2 wt.% [3] based on the water content in hydrous phases. Thus, slabs can carry H$_2$O into the mantle, which can affect geodynamics, such as seismicity, subduction processes, ascending plumes and magmatisms such as island arc volcanism, intraplate magmatism, hot spots and oceanic ridge magmatism. The average normal upper mantle is generally dry, as shown above, but the subducting slabs can carry a significant amount of water, in which two-thirds of the water dehydrates and generates magmas and triggers seismicity, whereas the rest can be stored in slabs and further carried into the deep mantle [3].

### A low-velocity region at the bottom of the upper mantle

Seismological studies reported the existence of low-velocity regions at the bottom of the upper mantle (~410-km depth) beneath Japan and northeast China [9], Europe [10] and the USA [11]. These regions might be caused by the existence of dense, volatile-rich magmas (e.g. [12]). Fig. 1 shows the phase and melting relations of wet peridotite at high pressure and temperature [13,14]. This figure shows a kink in the solidus curve near the 410-km discontinuity. This kink could be caused by the olivine–wadsleyte transformation with the water-solubility contrast between the two phases. Dehydration melting of plumes ascending from the

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**Table 1. Summary of the water contents in the mantle deduced by geophysical observations.**

| Mantle zone          | Water budget             | Water content                                                                 |
|----------------------|--------------------------|------------------------------------------------------------------------------|
| Upper mantle         | ~0.04 Ocean Mass         | <100 ppm of water in normal mantle: Electrical conductivity [4]              |
| Mantle transition    | 0.2–1 Ocean mass (assuming Wet TZ 30%; Dry TZ 70%) | 0.1–0.3 wt.% water in Pacific region based on electrical conductivity [5] |
| Lower mantle         | < 2 Ocean mass           | > 0.1 wt.% beneath eastern Asia, oversaturated in water locally [30]         |

0.01 wt.% Electrical conductivity [3]  
0.1 wt.% water based on electrical conductivity [5]  
0.2–2 wt.% water beneath Japan based on electrical conductivity and seismic tomography [61]  
0.5–1 wt.% water beneath Pacific based on electrical conductivity and seismic tomography [22]  
< 0.1 wt.% water beneath Europe by electrical conductivity and seismic tomography [22]  
1 wt.% beneath western Pacific based on topography of the 410 and 660 km discontinuities [62]  
ge < 0.1 wt.% water in normal lower mantle [30]
lower mantle could occur at ~410-km discontinuity. Fig. 2a and b shows the partial molar volumes of H$_2$O and CO$_2$ in magmas at high pressure and the density of the volatile-rich magmas [12,15]. The density of volatile-rich magmas has been studied by various authors using the in situ X-ray absorption method, sink-float method and ab initio calculations (e.g. [12,16]). Fig. 2a clearly indicates that H$_2$O is more compressible compared to CO$_2$ at high pressure and ~2000 K; and a rapid densification of hydrous melts occurs at the pressure and temperature conditions representative of the base of the upper mantle, suggesting the possible existence of dense hydrous magmas. Fig. 2b shows the density of volatile-rich magmas at high pressure and 1873 K, which clearly indicates that the wet ultramafic magmas with the H$_2$O content <5 wt.% is denser than the mineral assemblage at the bottom of the upper mantle, indicating the existence of gravitationally stable dense hydrous magmas along the plume geotherm.

### Hydrated mantle transition zone and existence of crust components

Recycling of the crustal components has been intensively studied in tectonics, geochemistry, petrology and geodynamics (e.g. [17,18]). The slabs are mainly composed of lithospheric components such as harzburgites, basalts, and continental and oceanic sediments [19].

Phase Egg, phase δ-AlO$_2$H [20] and hydrous ringwoodite, namely spinel type of Mg$_2$SiO$_4$ containing water up to 1 wt.% [21], have been discovered as inclusions in diamonds. These observations suggest that the mantle transition zone is wet locally. Geophysical observations such as electrical conductivity and seismic tomography also suggest that the mantle transition zone is wet at least locally [22].

Continental and oceanic sediment components might be transported into the mantle transition zone. The fingerprints of sediment components have been reported from C and N isotopes of eclogitic diamond grains [23]. Hydrous minerals, such as phase Egg and phase δ-AlO$_2$H stable under the transition-zone conditions [24,25] and TAPP (tetragonal almandine-pyrope phase) [26] might also be fingerprints of the crustal component included in diamond.

The crustal component subducted into the transition zone was modeled as a megolith by Ringwood [19]. The sediment component contains water as hydrous minerals such as phengite [27]. The existence of the component was suggested also by Kawai et al. [28]. The continental crustal materials can descend into the mantle transition zone, since silica minerals in this component transform to stishovite and the crustal materials become denser than the surrounding mantle materials [19]. Such continental crustal materials might play important roles as heat sources together with water carriers [27]: that is, the continental crustal materials contain a large amount of radiogenic elements such as K, U and Th, several hundred times higher than those of the surrounding mantle, and thus they may play a key role for heating the transition zone, upwelling and the generation of plumes [29].

### ROLE OF WATER IN THE LOWER MANTLE

#### Origin of the low V$_s$ and Q region at the top of the lower mantle

Lawrence and Wysession [30] reported the global attenuation pattern around the subducting slabs,
indicating the lowest Q anomaly in the shallow lower mantle beneath Eastern Asia. Schmandt et al. [31] reported the existence of a low Q and low V$_s$ region at the shallow lower mantle where volatile-rich magmas might be located. Recently, Sakamaki [32] argued a possibility that the dense hydrous magmas may exist at the bottom of the transition zone. A large compressibility of H$_2$O in magmas reduces the volume of wet magmas, resulting in a negligible volume difference between the dry and wet magmas as shown in Fig. 2a. Then the density difference between the dry and wet magmas at pressures >20 GPa becomes significantly smaller than that at lower pressures, as shown in Fig. 2b. Based on these experimental data, Sakamaki [32] showed that the density of wet magmas containing water < 8 wt.% may be greater than that of the preliminary reference Earth model (PREM) at 24 GPa and 1870 K—that is, the density crossover may exist at the bottom of the transition zone along the average temperature profile of the mantle [33].

Dense magmas, however, may not exist at the bottom of the transition zone. Fig. 1 shows the phase and melting relations of the hydrous peridotite (e.g. [13,14]). This figure indicates that the dehydration of slabs occurs at the bottom of the transition zone because of a strong contrast of H$_2$O contents between ringwoodite in the transition zone and bridgmanite and ferropericlase in the lower mantle, and dehydration of superhydrous phase B and phase D in the upper part of the lower mantle. Although the wet magmas containing ∼30 wt.% water have a low density relative to the surrounding mantle and move upwards due to buoyancy, continuous descent of the slabs causes dehydration, which can create a low Q and V$_s$ region at the boundary between the transition zone and the lower mantle, even in the absence of dense magmas.

The idea that hydrous magmas containing 2–8 wt.% H$_2$O are denser than the surrounding mantle along the normal mantle temperature estimated by Sakamaki [32] may contradict with the melting and phase relations of hydrous CMAS (CaO–MgO–Al$_2$O$_3$–SiO$_2$) pyrolite [13] and those of CFMAS (CaO–FeO–MgO–Al$_2$O$_3$–SiO$_2$) harzburgite [14]. The liquidus curve of pyrolite containing 2 wt.% water locates at 2400–2500 K and the partial melt contains 10 wt.% water at 2300 K at the base of the transition zone as shown in Fig. 1. Thus, the hydrous melts containing 8 wt.% water are formed above 2300 K, suggesting that such hydrous melts cannot exist along the normal mantle geotherm of 1870 K that was proposed by Sakamaki [32]. Zhang et al. [14] reported that the partial melt formed by the melting of the hydrous CFMAS harzburgite contains 30 wt.% of water at 20–22 GPa and 1700 K (Fig. 1). Very high temperatures above 2320 K are necessary for the generation of partial melts with 8 wt.% water, assuming hydrous harzburgite [14] has the same liquidus temperature as that of hydrous pyrolite [13]. The phase relations suggest that temperatures ∼400–500 K higher than the normal mantle geotherm are required to produce the hydrous magmas denser than the surrounding mantle at the bottom of the transition zone. Only the hot plumes ascending from the lower mantle would create such high temperatures.

The temperature profile of the lower mantle is uncertain—that is, compositional heterogeneities or stratification in the mantle could provide different temperature profiles to account for the density and velocity distribution of the lower mantle. Separate convection in the upper and lower mantles would create a thermal boundary in the mantle transition zone [34,35]. Counter flows due to the descent of the cold subducting slabs can create the ascent of the hot plumes surrounding the slabs. Therefore, the low Q and Vs region between the transition zone and the lower mantle may be explained by the continuous dehydration and fluid supply due to subduction along the low-temperature slab geotherm. However, we cannot rule out a possibility that the region is caused by the existence of dense hydrous melts at very high temperature due to the ascending plumes from the lower mantle caused by the counter flow generated by slab subduction.

![Figure 2](https://academic.oup.com/nsr/article/7/1/224/5514012)
Table 2. Hydrous phases stable under the lower-mantle conditions.

| Mineral                | Formula                        | Mg/Si | H₂O wt.%   | Reference |
|------------------------|--------------------------------|-------|------------|-----------|
| Superhydrous phase B = phase C | Mg₁₀Si₁₂(OH)₄ | 3.3   | 5.8        | [63]      |
| Phase D = phase F = phase G | Mg₁₁₋₄(Si₁₋₃)H₂₋₁O₆ | 0.66  | 14.5–18    | [63,64]   |
| Phase Egg              | Al₂SiO₅OH                  |       | 7.5        | [65]      |
| Phase δ                | Al₂O₅H                     |       | 15.0       | [66]      |
| Phase H                | MgSiO₅H₂                   |       | 15.2       | [67]      |
| Phase δ–H solid solution | (MgO₀.⁷SixO₀.⁷AI₀.₆xO₂H) | ~1   | 12.8       | [68,69]   |
| Pyrite-type FeO₂Hₓ     | FeO₂Hₓ                      | x = 0.39–1 |          | [70,71]   |
| HH phase               | (FeAI)O₂Hₓ                  |       | x ~ 1?     | [72]      |

Stability of hydrous δ-H solid solution, AlO₂H–MgSiO₄H₂

The existence of hydrous minerals in diamond [20,21] supports the locally hydrated mantle transition zone. The descent of the stagnant slabs can carry water farther into the lower mantle [36]. Table 2 summarizes the hydrous phases stable in the lower mantle.

The δ-H solid solution AlO₂H–MgSiO₄H₂ is a major carrier of water into the deep lower mantle. Sano et al. [25] and Duan et al. [37] showed that hydrous δ-AlO₂H is stable to the bottom of the lower mantle due to a strong O–H bonding caused by the hydrogen-bond symmetrization as discussed below. Recently, Yuan et al. [38] reported that the δ-H solid solution containing an FeO₂H component also is stable to the bottom of the lower mantle. The phase H, MgSiO₅H₂ was discovered recently and its stability field has been studied by various authors [39–41]. Fig. 3 shows the stability conditions of hydrous phases stable in the lower mantle such as phase D, phase δ, phase H and δ-H solid solution. Phase H is stable to 60 GPa and at temperatures <1600 K [40], as shown in this figure. It has an orthorhombic symmetry with a space group Pnmm, the same as that of δ-AlO₂D and δ-AlO₂H at >10 GPa [42].

The coexistence of bridgmanite/post-perovskite and δ-H solid solution can modify the alumina contents of bridgmanite and post-perovskite, the major minerals in the lower mantle. Fluids dehydrated at the top of the lower mantle react with alumina bridgmanite along the geotherms of the slab and normal mantle to create alumina-depleted bridgmanite coexisting with the phase δ-H solid solution. The partition coefficient of alumina D₃/Br or PP is very large, at ~14–26, in a wide pressure and temperature range. The Al₂O₃ contents of bridgmanite in MORB and peridotite under the dry condition are ~15 and ~5 wt.%, respectively [43], whereas the Al₂O₃ contents decrease significantly to ~3 and ~1 wt.%, respectively, by the addition of water and the formation of the hydrous phase due to a large partition coefficient of alumina between hydrous δ-H solid solution and bridgmanite.

Recent works on the stability of δ-phase in the MFASH (MgO–Fe₂O₃–Al₂O₃–SiO₂–H₂O) system showed the stability of the δ-phase in an iron-bearing system in the lower mantle and a strong partitioning of Al₂O₃ into the iron-bearing δ-phase coexisting both with bridgmanite and the post-perovskite phase [38]. Depletion of Al₂O₃ in bridgmanite and post-perovskite under the wet conditions provides effects on mantle dynamics due to the modification of the phase relations—that is, the Al₂O₃ depletion in bridgmanite lowers the pressure of the garnet–perovskite transition in MORB [43]. The depletion of Al₂O₃ also lowers the post-perovskite transition pressure and sharpens the phase transition at the base of the lower mantle.

Hydrogen-bond symmetrization in high-pressure hydrous phases

Hydrous phases such as phase δ [44] and phase D [45], stable in the lower mantle, have a strong and stable O–H bonding under high-pressure conditions because of hydrogen-bond symmetrization. Because of this bonding nature, the hydrous phases become stable and show elastic hardening at high pressure. The relation between O–H and O–Obond lengths due to the symmetrization of the O–H bond is shown in Fig. 4. The hydrogen-bond symmetrization has been observed in polymorphs of water ice. An inflection in the compression curves expressed by the Vinet equation of the state has been reported by Wolanin et al. [46] and Pruzan et al. [47] at 66 GPa for H₂O and 84 GPa for D₂O. This inflection can be explained by proton disordering—a signature of hydrogen-bond symmetrization. Elastic hardening due to hydrogen-bond symmetrization has been observed by Tsuchiya et al. [45] and Hushur et al. [48] in hydrous phase D.
They reported an increase in the bulk modulus, \( K_T \), from 173(2) to 212(15) GPa for hydrous phase D at ambient temperature due to hydrogen-bond symmetrization.

Tsuchiya et al. [49] showed by \textit{ab initio} calculations that both the P- and S- velocities of \( \delta\text{-AlO}_2\text{H} \) increase with increasing pressures to the mantle transition-zone conditions, becoming faster than those of wadsleyite, ringwoodite and majorite, in the mantle transition zone, and are comparable to those of bridgmanite at the shallow lower mantle. A strong O–H bond due to the hydrogen-bond symmetrization accounts for a high sound velocity of \( \delta\text{-AlO}_2\text{H} \).

A high sound velocity of \( \delta\text{-AlO}_2\text{H} \) comparable to bridgmanite by the hydrogen-bond symmetrization has strong implications for the role of water in the lower mantle. Phase H, \( \text{MgSiO}_4\text{H}_2 \) and phase \( \delta\text{-H} \) solid solution are considered to have high seismic velocities comparable to bridgmanite because of a structural similarity to \( \delta\text{-AlO}_2\text{H} \). Thus, it might be difficult to detect the existence of these hydrous phases in the shallow lower mantle by seismology.

In the previous sections, we learned that hydrous phase \( \delta\text{-H} \) solid solution, \( \text{AlO}_2\text{H}–\text{MgSiO}_4\text{H}_2 \), is the most important carrier of water in the slabs descending into the lower mantle [25,50]. This phase is expected to be dehydrated to produce fluids due to a steep geothermal profile at the CMB. Fluids generated by this process can hydrate the surrounding mantle at the base of the lower mantle and hydrated regions may create LLSP (low shear velocity province). The dehydration of \( \delta\text{-AlO}_2\text{H} \) occurs at \( \sim 2400 \text{ K} \) [25,37] at the base of the lower mantle, and dissolution of phase H component (\( \text{MgSi}_2\text{O}_4\text{H}_2 \)) further lowers the decomposition temperature [40], whereas pyrite \( \text{FeO}_2\text{H} \) seems to decompose to post-perovskite \( \text{Fe}_2\text{O}_3 \) and fluid at higher temperatures \( > 2500 \text{ K} \) [39], although the phase boundary is not yet determined precisely. Thus, the fluids generated by the decomposition of the \( \delta\text{-H} \) solid solution may react with iron from the core to create an iron hydrate \( \text{FeO}_2\text{H}_x \), which can cause the seismic anomaly of the ULVZ (ultralow velocity zone), as was suggested by Liu et al. [51] and Yuan et al. [52]. The processes expected at the bottom of the mantle are schematically shown in Fig. 5.
Pyrite structure FeO$_2$ (Pa3) was recently discovered as a reaction product between hematite and oxygen under the condition of 76 GPa and 1800 K [53]. Hu et al. [54] reported the formation of pyrite-type FeO$_2$H$_x$ based on their experimental results with scattered unit-cell volume values of pyrite FeO$_2$H$_x$ at a constant pressure and ab initio calculation. Nishi et al. [39] also reported FeO$_2$H pyrite by experiments and theoretical calculations suggesting the phase is close to stoichiometric, $x \sim 1$

Yuan et al. [52] reported that the iron–water reaction produces FeO and FeH$_x$ ($x \sim 78$ GPa, whereas FeO$_2$H$_x$ and FeH$_x$ (hcp and dhcp) were formed above 78 GPa at $\sim 2000$ K. The volumes of FeO$_2$H$_x$ reported by Yuan et al. [52] was comparable to that of stoichiometric pyrite FeO$_2$H$_x$ [55]—that is, the formation of nearly stoichiometric pyrite FeO$_2$H$_x$ with $x \sim 1$. Liu et al. [51] identified the iron–water reaction to form pyrite FeO$_2$H$_x$ and fcc-FeH$_x$ after quenching at 86 GPa.

The seismic velocities, $V_P$, $V_S$ and $V_\phi$, are significantly smaller than those of the lower-mantle minerals such as ferropericlase, bridgmanite and post-perovskite [51,52]. $V_\phi$ of pyrite FeO$_2$H$_x$ is 10% smaller than that of PREM [56] at the bottom of the mantle. Therefore, it may be a candidate for the ULVZ [52,53]. The high-pressure polymorph of Fe$_2$O$_3$ with a post-perovskite structure can be formed by the dehydration of pyrite FeO$_2$H$_x$ [39]. Therefore, post-perovskite Fe$_2$O$_3$ also can be a candidate phase for the ULVZ. Decomposition of pyrite FeO$_2$H$_x$ at the bottom of the mantle because of its dynamic instability could create global geological events, such as the Great Oxidation Event [57]. Recently, a new high-pressure form of AlO$_2$H–FeO$_2$H solid solution with a hexagonal symmetry has been reported at the base of the lower mantle [58]. This phase might be a potential water reservoir at the CMB regions. Further studies should be conducted to confirm the reservoir phases of water and to test the hypothesis of the generation of H$_2$ and O$_2$ at the bottom of the mantle [57].

**CONCLUSIONS**

Seismic and electrical conductivity observations combined with experimental mineral physics data on the sound velocity and electrical conductivity of minerals suggest the transition zone that is hydrated at least locally (e.g. [22]). Continental and oceanic sediment components together with the basaltic and peridotite components might be stored in the mantle transition zone (e.g. [19]). Low seismic velocity regions have been reported at $\sim 410$ km beneath some plate convergent regions (e.g. [9]). These regions might be caused by the existence of dense, volatile-rich magmas.

Water can be carried farther into the lower mantle by the descent of the slabs due to gravitational instability. The anomalous Q and $V_\phi$ regions might be created at the top of the lower mantle. Dehydration from the slabs produces fluids or hydrous melts in this region due to a large difference in the water solubility between the transition zone and the lower mantle assemblages (e.g. [59]). Although hydrous magmas without density crossover can escape upwards, continuous descent of the slabs causes dehydration from the slabs and produces low Q and $V_\phi$ regions at the shallow part of the lower mantle. δ-H solid solution AlO$_2$H–MgSiO$_2$H$_2$ is a major carrier of water into the lower mantle. The hydrogen-bond symmetrization could occur in various hydrous phases stable in the mantle (e.g. [44]).

The CMB is a region where extensive reaction between water and iron might occur. The δ-H solid solution is stable to the CMB conditions. Therefore, this hydrous phase carries water into the base of the lower mantle and also into the core. Pyrite FeO$_2$H$_x$ can be formed due to a reaction between the core and hydrated slabs at the CMB. This phase could be a potential candidate existing at the ULVZ [51,52]. Formation of FeO$_2$H$_x$ and its decomposition due to its thermal instability at the CMB could cause global geodynamical events [57].

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**REFERENCES**

1. Peacock SM. Fluid processes in subduction zones. *Science* 1990; 248: 329–37.

2. Wallace PJ. Volatiles in subduction zone magmas: concentrations and fluxes based on melt inclusion and volcanic gas data. *J Volcanol Geotherm Res* 2005; 140: 217–40.

3. van Keken PE, Hacker BR and Syracuse EM. Factory: Depth-dependent flux of H2O from subducting slabs worldwide. *J Geophys Res* 2011; 116: 401.

4. Khan A and Shankland TJ. A geophysical perspective on mantle water content and melting: inverting electromagnetic sounding data using laboratory-based electrical conductivity profiles. *Earth Planet Sci Lett* 2012; 317–318: 27–43.

5. Karato S. Water distribution across the mantle transition zone and its implications for global material circulation. *Earth Planet Sci Lett* 2011; 301: 413–23.

6. Kolesnichenko MV, Zedgenizov DA and Litasov KD et al. Heterogeneous distribution of water in the mantle beneath the central Siberian Craton: implications from the Udachnaya Kimberlite Pipe. *Gondwana Res* 2017; 24: 49–66.

7. Doucot LS, Peslier AH and Ionov DA et al. High water contents in the Siberian cratonic mantle linked to metasomatism: an FTIR study of Udachnaya peridotite xenoliths. *Geochim Cosmochim Acta* 2014; 137: 159–87.

8. Dixon JE, Leist L and Langmuir C et al. Recycled dehydrated lithosphere observed in plume-influenced mid-ocean-ridge basalts. *Nature* 2002; 420: 385–9.

9. Revenaugh J and Sipkin SA. Seismic evidence for silicate melt atop the 410-km mantle discontinuity. *Nature* 1994; 369: 474–6.

10. Nolet G and Zielhaus A. Low S velocities under the Tornquist-Zeiss zone: evidence for water injection into the transition zone by subduction. *J Geophys Res* 1994; 99: 15813–20.

11. Song TRA, Heimberger DV and Grand SP. Low-velocity zone at the 410-km seismic discontinuity in the northwestern United States. *Nature* 2004; 427: 530–3.

12. Sakamaki T, Ohtani E and Urakawa S et al. Measurement of hydrous peridotite magma density at high pressure using the X-ray absorption method. *Earth Planet Sci Lett* 2009; 287: 293–7.

13. Litasov KD and Ohtani E. Phase relations and melt compositions in CMAS–pyroilite–H2O system up to 25 GPa. *Phys Earth Planet Inter* 2002; 134: 105–27.

14. Zhang Y, Wang C and Jin Z et al. Partial melting of stagnant oceanic lithosphere in the mantle transition zone and its geophysical implications. *Lithos* 2017; 92–93: 379–87.

15. Sakamaki T, Ohtani E and Urakawa S et al. Density of carbonated peridotite magma at high pressure using an X-ray absorption method. *Am Mineral* 2011; 96: 553–7.

16. Bajgian S, Ghosh DB and Karki BB. Structure and density of basaltic melts at mantle conditions from first-principles simulations. *Nat Commun* 2015; 6: 8578.

17. Ringwood AE, Kesson SE and Hibberson W et al. Origin of kimberlites and related magmas. *Earth Planet Sci Lett* 1992; 113: 521–38.

18. Duca MN. Understanding continental subduction: a work in progress. *Geology* 2016; 44: 239–40.

19. Ringwood AE. Phase transformation and differentiation in subducted lithosphere: implications for mantle dynamics, basalt petrogenesis and crustal evolution. *J Geol* 1982; 90: 611–43.

20. Wirth R, Vollmer C and Brenker F et al. Inclusions of nanocrystalline hydrous aluminium silicate ‘phase Egg’ in superdeep diamonds from Juina (Mato Grosso State, Brazil). *Earth Planet Sci Lett* 2007; 259: 384–99.

21. Pearson DG, Brenker FE and Nestola F et al. Hydrous mantle transition zone indicated by ringwoodite included within diamond. *Nature* 2014; 507: 221–4.

22. Utada H, Koyama T and Obayashi M et al. A joint interpretation of electromagnetic and seismic tomography models suggests the mantle transition zone below Europe is dry. *Earth Planet Sci Lett* 2009; 281: 249–57.

23. Cartigny P. Stable isotopes and the origin of diamond. *Elements* 2005; 1: 79–84.

24. Sano A, Ohtani E and Kubo T et al. Measurement of high water contents and melting at the top of the lower mantle. *Earth Planet Sci Lett* 2015; 427: 105–27.

25. Sano A, Ohtani E and Kondo T. Aluminum oxide hydroxide d-AlOOH at high pressure and temperature. *Am Mineral* 2011; 96: 15813–20.

26. Nestola F, Burnham AD and Peruzzo L et al. Tetragonal Almandine-Pyrope Phase, TAPP: finally a name for it, the new mineral jeffbenite. *Mineral Mag* 2016; 80: 1219–32.

27. Ono S. Stability limits of hydrous minerals in sediment and mid-ocean ridge basalt compositions: implications for water transport in subduction zones. *J Geophys Res* 1998; 103: 18253–67.

28. Kawai K, Tsuchiya T and Maruyama S. The second continent (in Japanese with English abstract). *Jour Geography (Chigaku Zasshi)* 2010; 119: 1197–214.

29. Schmandt B, Jacobsen S and Becker TW et al. Dehydration melting at the top of the lower mantle. *Science* 2014; 344: 1265–8.
32. Sakamaki T. Density of hydrous magma. *Chem Geol* 2017; 475: 135–9.
33. Katsura T, Yoneda A and Yamazaki D et al. Adiabatic temperature profile in the mantle. *Phys Earth Planet Inter* 2010; 183: 212–8.
34. da Silva CRS, Wentzczovitch RM and Patel A et al. The composition and geotherm of the lower mantle: constraints from the elasticity of silicate perovskite. *Phys Earth Planet Inter* 2009; 118: 103–9.
35. Spiliopoulos S and Stacy FD. The Earth’s thermal profile: is there a mid-mantle thermal boundary layer? *J Geodyn* 1984; 1: 61–77.
36. Ohtani E. Water in the mantle. *Elements* 2005; 1: 25–30.
37. Duan Y, Sun N and Wang S et al. Phase stability and thermal equation of state of δ-AlOOH: implication for water transportation to the deep lower mantle. *Earth Planet Sci Lett* 2018; 494: 92–8.
38. Yuan H, Zhang L and Meng Y et al. The stability of Fe-bearing δ-phase and pyrite-phase FeO2H2 in the Earth’s lowermost mantle: experimental constrains from a hydrated FeAI-bearing MgSiO3 composition. *Abstract MR23B-0088 presented at 2018 Fall Meeting, Washington, DC. AGU, 10–14 December.*
39. Nishi M, Kuwayama Y and Tsuchiya J et al. The pyrite-type high-pressure form of FeO2H. *Nature* 2017; 547: 205–8.
40. Ohtani E, Amaike Y and Kamada S et al. Stability of hydrous phase H MgSiO3H2 under lower mantle conditions. *GeoRes Lett* 2014; 41: 8283–7.
41. Walter MJ, Kohn SC and Araujo D et al. Deep mantle cycling of oceanic crust: evidence from diamonds and their mineral inclusions. *Science* 2011; 334: 54–7.
42. Bind L, Nishi M and Tsuchiya J et al. Crystal chemistry of dense hydrous magnesium silicates: the structure of phase H, MgSi2O4H2, synthesized at 45 GPa and 1000°C. *Am Mineral* 2014; 99: 1802–5.
43. Irifune T and Tsuchiya T. Phase transitions and mineralogy of the lower mantle. In: Schubert G, ed. *Treatise on Geophysics*, 2nd edn. Amsterdam: Elsevier, 2015; 2, Chap. 2, 03, 33–60.
44. Sano-Furukawa A, Kagi H and Nagai T et al. Change in compressibility of δ-AlOOH and δ-AlO2D at high pressure: a study of isotope effect and hydrogen-bond symmetrization. *Am Mineral* 2009; 94: 1255–61.
45. Tsuchiya J, Tsuchiya T and Tsuneyuki S. First-principles study of hydrogen bond symmetrization of phase D under high pressure. *Am Mineral* 2005; 90: 44–9.
46. Wolanin E, Pruzan PHC and Chervin JC et al. Equation of state of ice VII up to 106 GPa. *Phys Rev B* 1997; 56: 5781–5.
47. Pruzan PJ, Cherivin JC and Wolanin B et al. Phase diagram of ice in the VII–VIII–X domain: vibrational and structural data for strongly compressed ice VIII. *J Raman Spectrosc* 2003; 34: 591–160.
48. Hushur A, Manghmani MH and Smyth JR et al. Hydrogen bond symmetrization and equation of state of phase D. *J Geophys Res* 2011; 116: B6.
49. Tsuchiya J, Tsuchiya T and Wentzczovitch RM. Vibrational properties of δ-AlOOH–MgSiO3(OH)– and a mechanism of water transport into the base of lower mantle. *Earth Planet Sci Lett* 2014; 401: 12–7.
50. Liu J, Hu Q and Kim DY et al. Hydrogen-bearing iron peroxide and the origin of ultralow-velocity zones. *Nature* 2017; 551: 494–7.
51. Yuan L, Ohtani E and Ikuta D et al. Chemical reactions between Fe and H2O up to megabar pressures and implications for water storage in the Earth’s mantle and core. *Geophys Res Lett* 2018; 45: 1330–8.
52. Hu Q, Kim DY and Yang W et al. FeO2 and FeO2H under deep lower-mantle conditions and Earth’s oxygen–hydrogen cycles. *Nature* 2016; 534: 241–4.
53. Ohtani E, Yuan L and Ohira I et al. Dehydrogenation of goethite in Earth’s deep lower mantle. *Proc Natl Acad Sci USA* 2017; 114: 494–501.
54. Nishi M, Irifune T and Tsuchiya J et al. Stability of hydrous silicate at high pressures and water transport to the deep lower mantle. *Nat Geosci* 2014; 7: 224–7.
55. Dziewonski AM and Anderson DL. Preliminary reference earth model. *Phys Earth Planet Inter* 1981; 25: 297–356.
56. Zhang L, Yuan H and Meng Y et al. Discovery of a hexagonal ultradense hydrous phase in (Fe,Al)O(OH). *Proc Natl Acad Sci USA* 2018; 115: 2908–11.
57. Ohtani E, Yuan L and Ohira I et al. Fate of water transported into the deep lower mantle by slab subduction. *J Asian Earth Sci* 2018; 167: 2–10.
58. Yoshino T, Manthilake G and Matsuozaki T et al. Dry mantle transition zone inferred from the conductivity of wadsleyite and ringwoodite. *Nature* 2008; 451: 326–9.
59. Koyama T, Shimizu H and Utada H et al. Water contents in the mantle transition zone beneath the north Pacific derived from the electrical conductivity anomaly. In: Jacobsen SD and Van der Lee S (eds). *Earth’s Deep Water Cycle*. Geophysical Monograph Series 168. Washington, DC: American Geophysical Union, 2006, 171–9.
60. Suetsugu D, Inoue T and Obayashi M et al. Depths of the 410-km and 660-km discontinuities and in and around the stagnant slab beneath the Philippine Sea: is water stored in the stagnant slab? *Phys Earth Planet Inter* 2010; 183: 270–9.
61. Gasparik T. Phase relations in the transition zone. *J Geophys Res.* 1990; 95: 15751–69.
62. Ohtani E, Kudoh Y and Naito H et al. Stability of dense hydrous magnesium silicate in the transition zone and the lower mantle. *Mineral J* 1998; 9: 163–9.
63. Egginton RA, Board NJ and Ringwood AE. High pressure synthesis of a new alumina silicate: Al2Si2O7(OH). *Geochim J* 1978; 12: 191–4.
64. Suzuki A, Ohtani E and Kamada T. A new hydrous phase δ-AlO2D synthesized at 21 GPa and 1000°C. *Phys Chem Miner* 2000; 27: 689–93.
65. Kennett BLN, Engdahl ER and Buland R. Constraints on seismic velocities in the Earth from traveltimes. *Geophys J Int* 1995; 122: 108–24.
66. Sano-Furukawa A, Komatsu K and Vanpeteghem CB et al. Neutron diffraction study of δ-AlO2D at high pressure and its implication for symmetrization of the hydrogen bond. *Am Mineral* 2008; 93: 1558–67.
67. Tsuchiya J, Tsuchiya T and Tsuneyuki S et al. First principles calculation of a high-pressure hydrous phase, δ-AlOOH. *Geophys Res Lett* 2002; 29: 1909.
68. Nelmes RJ, Loveday JS and Wilson RM et al. Neutron diffraction study of the structure of deuterated ice VII to 10 GPa. *Phys Rev Lett* 1993; 71: 1192–5.
69. Nelmes RJ, Loveday JS and Marshall WG et al. Structures of Ice VII and Ice VIII to 20 GPa. *The Rev High Pres Sci Tech* 1998; 7: 1138–40.