

GEOSCIENCES

Distribution, cycling and impact of water in the Earth's interior

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ABSTRACT

The Earth's deep interior is a hidden water reservoir on a par with the hydrosphere that is crucial for keeping the Earth as a habitable planet. In particular, nominally anhydrous minerals (NAMs) in the silicate Earth host a significant amount of water by accommodating H point defects in their crystal lattices. Water distribution in the silicate Earth is highly heterogeneous, and the mantle transition zone may contain more water than the upper and lower mantles. Plate subduction transports surface water to various depths, with a series of hydrous minerals and NAMs serving as water carriers. Dehydration of the subducting slab produces liquid phases such as aqueous solutions and hydrous melts as a metasomatic agent of the mantle. Partial melting of the metasomatic mantle domains sparks off arc volcanism, which, along with the volcanism at mid-ocean ridges and hotspots, returns water to the surface and completes the deep water cycle. There appears to have been a steady balance between hydration and dehydration of the mantle at least since the Phanerozoic. Earth's water probably originates from a primordial portion that survived the Moon-forming giant impact, with later delivery by asteroids and comets. Water could play a critical role in initiating plate tectonics. In the modern Earth, the storage and cycling of water profoundly modulates a variety of properties and processes of the Earth's interior, with impacts on surface environments. Notable examples include the hydrolytic weakening effect on mantle convection and plate motion, influences on phase transitions (on the solidus of mantle peridotite in particular) and dehydration embrittlement triggering intermediate- to deep-focus earthquakes. Water can reduce seismic velocity and enhance electrical conductivity, providing remote sensing methods for water distribution in the Earth's interior. Many unresolved issues around the deep water cycle require an integrated approach and concerted efforts from multiple disciplines.

Keywords: water, Earth's interior, mantle, subduction, partial melting

INTRODUCTION

The Earth is a hydrous planet, and water is the most crucial resource for the emergence and well-being of humankind and other life forms. Although not immediately evident, a huge amount of water, perhaps several times the mass of the entire hydrosphere, is stored in the Earth's interior [1–3]. In particular, the mantle transition zone may be a gigantic water reservoir and contain much more water than the upper and lower mantles [4–6].

Alongside other chemical components, water on Earth's surface is carried by plate subduction into Earth's interior, probably down to the core–mantle boundary. In response to changes in temperature

(*T*) and pressure (*P*) along subduction paths, water is redistributed among coexisting mineral phases (including some that are newly formed) in subducting slabs [7–9]. On the other hand, the subducting slabs release some of their water, in the form of liquid phases such as aqueous solutions, hydrous melts and supercritical fluids, into the overlying mantle wedge [10–13]. The hydrated mantle domains are destined to partially melt over time, eventually evolving into volcanism. Volcanic eruptions at arcs along with those at mid-ocean ridges and hotspots return water to the Earth's surface. This grand journey of water transport into and out of the Earth's interior is commonly referred to as the deep water cycle [14].

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The storage and cycling of water has far-reaching impacts over geodynamic and geochemical evolution by modulating a variety of properties and processes of the Earth's interior [15–19]. Water probably played an indispensable role in the formation of continental crust [20] and in the initiation of subduction [21]. Dissolved water weakens the mechanical strength of olivine and other mantle minerals, thereby influencing mantle convection and plate tectonics [22–24]. Another well-known fact is that the melting temperatures of silicates are strongly depressed by the presence of water [23,25–27].

The significance of water in the Earth's evolution is increasingly appreciated by Earth scientists from multiple fields. Water in the solid Earth has come to be a frontier and hot topic of research over the past three decades. This review aims to provide a comprehensive yet concise summary of recent progress in our understanding of the speciation, distribution, cycling and impact of water in the Earth's interior.

THE HYDROUS SPECIES

All of the major phases in the Earth's interior take up some water, albeit in different forms. In aqueous solutions, the predominant hydrous species is molecular H_2O along with its dissociated forms (H_3O^+ and OH^-). In silicate melts, it is chiefly molecular H_2O or hydroxyl groups (OH) bonded to Si or other cations [28,29], but pressure of the order of 10 GPa gives rise to more extended structures such as $\text{Si}-\text{O}-\text{H}-\text{O}-\text{Si}$ [30] and low oxygen fugacity leads to molecular H_2 [31]. In stoichiometrically hydrous minerals such as amphiboles and dense hydrous magnesium silicates (DHMS), OH is an innate component of the crystal lattice [32]. In olivine and other nominally anhydrous minerals (NAMs), which constitute the main body of the bulk silicate Earth, hydrogen generally occurs in point defects and bonds to oxygen to form OH [33,34]. One exception is that the open structure of feldspars can accommodate H_2O molecules [35,36]. Mineral grains may also enclose fluid inclusions or other microscopic hydrous impurities, especially at shallow depths. In the reduced deep mantle, a fraction of hydrogen could dissolve into silicate minerals as molecular H_2 [37]. Hydrogen could be a minor element present in the core as iron hydrides [38,39]. These reduced hydrogen species and rare species such as NH_4^+ are beyond the scope of this review, and will be only gently touched upon below.

Throughout this review, the term water content always refers to the weight fraction of H_2O (in wt% or in ppm) converted from all of the hydrous species in existence. Fourier transform infrared spec-

troscopy is by far the most frequently used technique for determination of water content in oxide minerals and glasses [40–42]. Secondary ion mass spectrometry permits submicron spatial resolution [43], but is more technically challenging and is not routinely available. Other methods are even less commonly used at present.

THE RESERVOIRS

Water distribution in the Earth's interior is highly heterogeneous (Table 1; Fig. 1). The upper continental crust is estimated to contain several thousand ppm of water, mainly in hydrous minerals or as fluid inclusions in felsic minerals such as quartz and feldspars [36]. Studies of granulite xenoliths indicate that the lower continental crust is less hydrous, typically with several hundred ppm of water in NAMs [44]. The middle continental crust is generally characterized by the occurrence of amphibole and has water content that is intermediate between the upper and lower continental crusts.

The oceanic crust, composed of mafic igneous rocks and seafloor sediments, is much richer in water than the continental crust. The mafic crust, hydrothermally altered by seawater, contains 1.5 wt% water on average, as pore water or contained in hydrous minerals (including clay minerals) and NAMs [45]. However, the oceanic crust subducted to subarc depths is significantly dehydrated at forearc depths, and is essentially not much different from the continental crust subducted to similar depths with respect to water content [12,61].

Erupted basalts along with the mantle xenoliths they enclose indicate diverse water contents in the upper mantle. Water content of the subcontinental lithospheric mantle spans from almost completely dry to ~250 ppm [41,44,46,62]. The source regions of normal mid-ocean ridge basalts (MORBs), which probably represent a major part of the asthenospheric mantle, are estimated to contain 50–250 ppm water [47–49]. The source regions of ocean island basalts (OIBs), continental flood basalts and enriched MORBs, which may represent a minor portion of the asthenospheric mantle or may be more deeply located, are more hydrous than the normal MORB source, typically with 300–1000 ppm water [50,52,63]. At subduction zones, after being metasomatized by hydrous liquids derived from the subducting slab, the bulk water content of the mantle wedge may rise to a few wt% [53,54].

The major minerals in the transition zone (i.e. wadsleyite and ringwoodite) have long been known to be capable of accommodating a significant amount of water comparable with hydrous minerals

Table 1. Earth's water budget.

	Water content (ppm)	Main forms	Total amount of water (kg)	Relative to the hydrosphere
Hydrosphere	9.6×10^5	Liquid water; ice	1.4×10^{21}	1
Upper continental crust [36]	9×10^3	Hydrous minerals; fluid inclusions	6×10^{19}	0.04
Lower and middle continental crust [44]	$<1 \times 10^3$	NAMs; hydrous minerals	$<2 \times 10^{19}$	0.01
Oceanic crust [45]	1.5×10^4	Pore water; clay minerals; hydrous minerals; NAMs	1×10^{20}	0.07
Subcontinental lithospheric mantle [41,44,46]	<250	NAMs	$<1 \times 10^{19}$	<0.01
MORB source [47–49]	50–250	NAMs	1×10^{20}	0.07
OIB/flood basalt source [50–52]	300–1000	NAMs	$<1 \times 10^{19}$	<0.01
Metasomatic mantle [26,53,54]	3×10^3 – 4×10^4	Hydrous minerals; NAMs	$<1 \times 10^{19}$	<0.01
Transition zone [6,55]	1×10^4 ?	NAMs (ringwoodite; wadsleyite)	4.5×10^{21} ?	3 ?
Lower mantle [56–59]	1–4000	NAMs	3×10^{18} – 1×10^{22}	0.002–8
Core [39,60]	1×10^4 H?	FeH _x		

[5,64]. However, it was only recently that the first direct evidence, from a diamond-hosted ringwoodite inclusion, confirmed the transition zone to be, at least locally, hydrous [6]. If the inferred ~ 1 wt% water in ringwoodite was globally representative, the transition zone would be a gigantic water reservoir triple the size of the hydrosphere. However, there is geophysical evidence suggesting that the transition zone can also be locally dry [65].

The most controversial issue is the water content of the lower mantle. A number of experimental and computational studies suggest that bridgmanite, the major phase of the lower mantle, could accommodate 0.1–0.4 wt% water [56,57,59]. However, some other workers hold that the high water content found in quenched bridgmanite could be caused by mechanically trapped hydrous inclusions and that the intrinsic water storage capacity of bridgmanite is only a few ppm [58]. Consistent with the view of low water storage capacity of the lower mantle is the finding of H₂O-bearing fluids [66].

For NAMs or rocks, water storage capacity is the maximum amount of water that can be sequestered in the mineral(s) without stabilizing a hydrous fluid or melt phase [27,67]. Only at low temperature and pressure, when the mineral(s) coexist with aqueous solution with water activity ≈ 1 , should water

storage capacity be referred to as water solubility. The distinction between water storage capacity and water solubility is illustrated in Fig. 2 for the forsterite–H₂O system. A compilation of experimental studies on the water storage capacity of mantle minerals is available in Yang and Li [68]. These results establish a high bound for actual water content in a solid mantle.

ALONG THE SUBDUCTION PATH

Plate subduction is the predominant mechanism that delivers water into the Earth's interior [12,61]. With the increase of temperature and pressure along the subduction path, the subducting slab undergoes metamorphic dehydration, phase transformations, and even partial melting. Among other parameters, the thermal structure of subduction zones is pivotal in shaping the detailed processes at different depths [12,69,70].

The oceanic plate has stratified water contents. The overlying sedimentary layer, typically less than 1 km thick, is extremely water-rich, with 20–70 wt% H₂O [71]. The water content of the igneous portion decreases from ~ 10 wt% in the upper extrusive rocks to ~ 1 wt% in the gabbro layer [45]. The upper

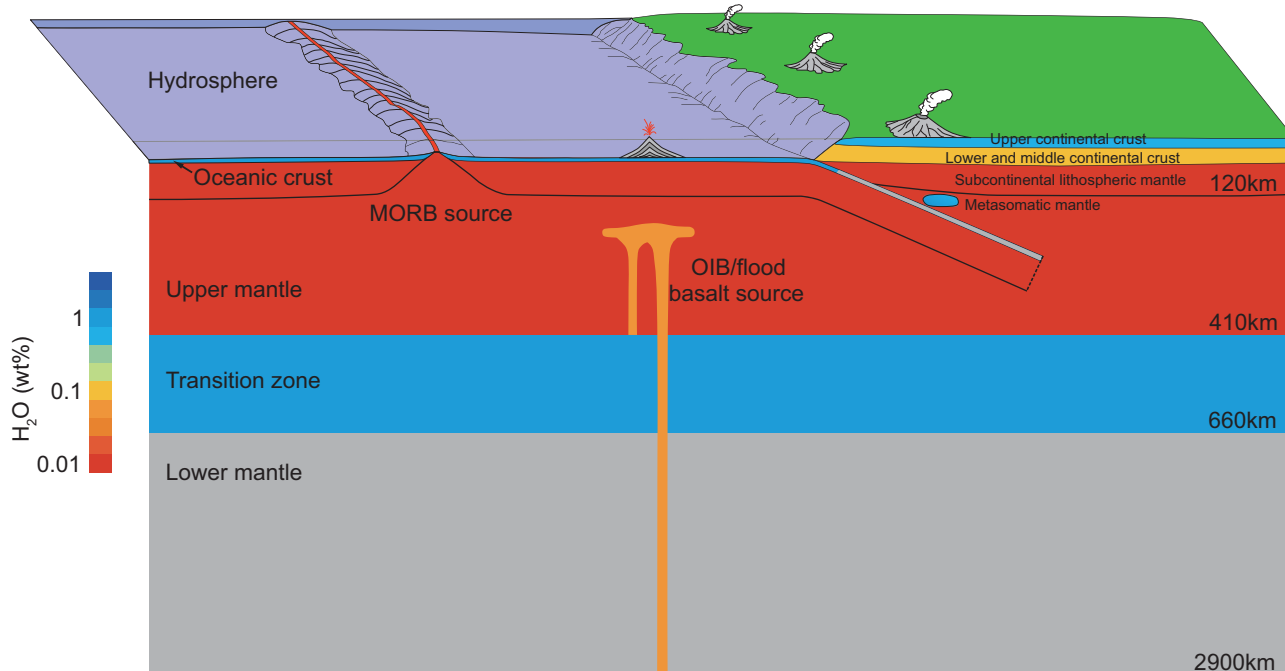


Figure 1. A simplified view of water distribution in the Earth's layered interior by neglecting intralayer heterogeneities, based on the data summarized in Table 1. The lower mantle is coded in grey due to its poorly constrained water content.

several km of lithospheric mantle peridotite can also experience significant hydrothermal alteration [72].

Due to compaction and heating, a significant amount of pore water in the upper oceanic crust is expelled from the slab during the initial stage of subduction. Approaching 300°C and 1 GPa, water is mainly stored in zeolite, prehnite and pumpellyite, and the bulk water content of the upper crust is 6–9 wt% [61,73]. Upon further *P-T* increase to around 600°C and 2.5 GPa (high-pressure blueschist to eclogite facies at the forearc depths, <80 km), the slab continues to dehydrate appreciably (Fig. 3). The major hydrous minerals include chlorite, amphibole, micas, and epidote, with lawsonite only stable for a cold subduction path [12]. Across the amphibole-out boundary, the bulk water content decreases from ~2 wt% to ~1 wt%, corresponding to a volume fraction increase of NAMs from ~50% to >70%.

Along a cold subduction path, the already highly-dehydrated oceanic crust enters a *P-T* regime (500–800°C and 2.5–10 GPa) with dehydration rates notably lower than at previous stages (Fig. 3). Furthermore, both the variety and abundance of hydrous minerals are significantly reduced, with the major phases including lawsonite, zoisite, chloritoid, talc and phengite. Increasing fraction of water is distributed in NAMs, and the bulk water content further drops to only a few 1000 ppm at the subarc (80–160 km) and postarc (>200 km) depths.

If subduction proceeds along a hot path (Fig. 3), the oceanic crust would plunge into the

melting regime (650–950°C and <5 GPa). Zoisite, amphibole and micas are the major water hosts, and the bulk water content remains >1 wt% before melting at *P* < 2.5 GPa (Fig. 3). At higher pressures, amphibole is no longer stable, resulting in a bulk water content of <1 wt% in the crust before melting. Despite the low water content in the crust, dehydration of the underlying peridotite could induce melting of the crust at 1–4 GPa and 650–850°C under water-saturated conditions. At temperatures above

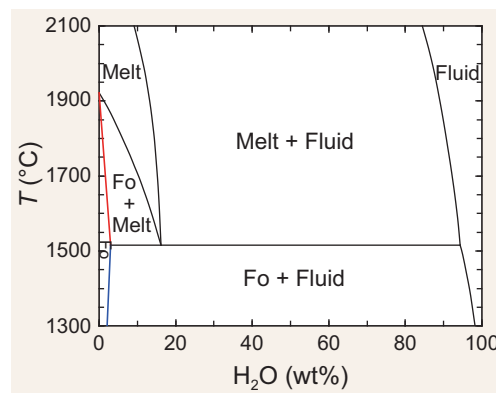


Figure 2. Phase diagram of forsterite (Fo)–H₂O at 1 GPa. The blue curve indicates water solubility in forsterite at low temperatures (saturated by aqueous solution) and the red curve indicates water storage capacity in forsterite at high temperatures (saturated by hydrous melt). These curves are exaggerated toward higher water content for clear demonstration. Modified from Ni *et al.* [27].

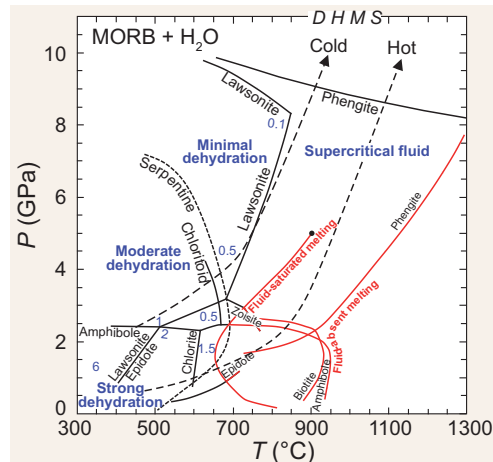


Figure 3. Dehydration and melting regimes of oceanic crust along cold and hot subduction paths (dashed curves with arrow) based on the mineral stability fields in the MORB–H₂O system. The numbers indicate the estimated bulk water content of the oceanic crust in wt%. DHMS (dense hydrous magnesium silicates) form at $P > 10$ GPa. The stability field of serpentine in peridotite is shown for comparison. Modified from Schmidt and Poli [8].

800–900°C, melting of the crust can occur at subarc depths even under water-undersaturated conditions. Partial melting of the oceanic crust gives rise to adakitic magmatism [74].

If a cold subduction path bypasses the wet solidus of crustal rocks (Fig. 3), which terminates at the second critical endpoint (perhaps 900°C and 5 GPa for the MORB–H₂O system but still controversial [75,76]), the subducting crust can release supercritical fluids with composition and physicochemical properties distinct from aqueous solutions (with >70 wt% H₂O) and hydrous silicate melts (with <30 wt% H₂O) [8,13,77–79].

The above discussion has focused on the oceanic crust. The overlying carbonated sediments could be melted at postarc depths of >200 km, producing hydrous silicate or carbonatite melts [80]. The total mass of water stored in the underlying serpentinized peridotite is difficult to estimate accurately, but may be comparable to that in the oceanic crust [8,72]. Dehydration of the serpentinized peridotite is insignificant below 3–6 GPa, with ~ 7 wt% water mainly hosted in serpentine and chlorite. Along the cold subduction path, serpentine breaks down to a series of DHMS (phases A, E, D and superhydrous phase B) at $P > 6$ GPa [32,81], but still up to 5 wt% water could be transported further down toward the transition zone [8]. Along a hot geotherm, serpentine transforms into the 10 Å phase or Mg-sursassite, during which significant dehydration lowers the bulk water content to only ~ 0.6 wt%.

Studies of seismic tomography reveal the presence of stagnant slabs in the transition zone below continental edges in the circum-Pacific areas [82–85]. The stagnant slab is thought to lose water to the transition zone and also to the overlying ‘big mantle wedge’ [86–89]. However, the detailed process of slab–mantle interaction at the transition zone and how this is linked to the origin of continental basalts are still poorly understood.

Some other slabs can subduct to much greater depths in the lower mantle. Water carriers in subducting slabs to the deep mantle are suggested to include superhydrous phase B, phase D, phase Egg, phase δ -H solid solution [32], (FeH)_{1-x}Ti_xO₂ [90], FeOOH [91], ringwoodite and other NAMs. Among these phases, ringwoodite, Al-rich phase D, and phase δ -H solid solution probably play more major roles than the others [32,92,93]. Due to the difference in water storage capacity between ringwoodite and lower mantle minerals, dehydration melting could occur at the top of the lower mantle [94,95]. Heating near the core–mantle boundary may lead to the breakdown of phase δ -H and melting of the slab [32]. In addition, Hu *et al.* [91] suggest that FeOOH could decompose to FeO₂ and H₂ at >1800 km depths, remolding the deep water cycle, which is challenged by the discovery of a pyrite-type high-pressure form of FeOOH [96].

A geodynamic model by van Keken *et al.* [70] estimates that globally subducting slabs carry $\sim 10^{12}$ kg/year of water into the Earth’s interior. One-third of it is lost by 100 km depth (i.e. at the forearc and subarc depths), another one-third is lost by 230 km depth, and the remaining one-third is transported into the Earth’s deeper interior.

FROM DEPTHS TO SURFACE

Buoyancy drives the hydrous liquid phases released by the subducting slab to migrate upward, in porous or channeled flow, to the overlying mantle wedge, leading to metasomatism [12,97]. Hydrous minerals in metasomatic mantle domains, with estimated bulk water content of 0.3–4 wt% [53,54], mainly include serpentine, talc, phlogopite and amphibole [8]. The mantle wedge probably starts to melt after a period of storage and heating [12]. Melt inclusion records suggest that water contents in primary mafic melts generally fall in the range of 2–6 wt%, although significantly higher or lower water contents have also been reported [26,98]. Water contents in the melts change continuously along the path of magma evolution and ascent, due to processes such as crustal contamination, magma mixing, and fractional crystallization.

Fractional crystallization of NAMs raises the concentration of volatiles in the melts, which along with pressure decrease leads to volatile saturation and the exsolution of magmatic–hydrothermal fluids, referred to as boiling [99]. At lower temperature and pressure, such hydrothermal fluids may further separate into a brine and a vapor phase, and these fluids play a critical role in the mobilization of metal elements and formation of ore deposits [100]. Alternatively, they may evolve into volcanic gases and reach Earth's surface. Wallace [101] suggests that the global flux of outgassing water through arc volcanism is $\sim 3 \times 10^{11}$ kg/yr, which approximates the amount of water loss by subducting slabs by 100 km depth and indicates a balance between subduction input and eruption output.

Water preserved in the slab beyond the subarc depths experiences more prolonged transport and evolution in the mantle. Some of it could be incorporated in the source regions of OIBs and enriched MORBs [63,102], or could replenish the normal MORB source unobtrusively. Bercovici and Karato [103] posit that due to the contrasting water storage capacities between the transition zone and upper mantle, dehydration melting at their boundary (410 km depth) would deprive the upwelling

mantle of most of its water and form the normal MORB source. The global flux of outgassing water through mid-ocean ridge volcanism is estimated to be $\sim 6 \times 10^{10}$ kg/yr [10], significantly lower than that through arc volcanism. Putting together these estimates of water fluxes [10,70,101], there appears to be more water going into than coming out of the Earth's interior at present. If this inference were true, the surface water reservoir would be shrinking over time. However, these global estimates are associated with large uncertainties. Furthermore, it is probably not appropriate to take the inferred contemporary water inventory as a long-term pattern over geological history.

Besides volcanic eruptions, the exhumation of ultrahigh-pressure metamorphic rocks, which is much more common for continental than for oceanic subduction zones [104,105], provides a direct means to return water from the Earth's interior to the surface [9]. On the other hand, lithospheric delamination also transfers minor amounts of water into the asthenospheric mantle. However, in general, plate subduction and volcanism are by far the most predominant mechanisms for the input and output of water in the deep water cycle, as illustrated in Fig. 4.

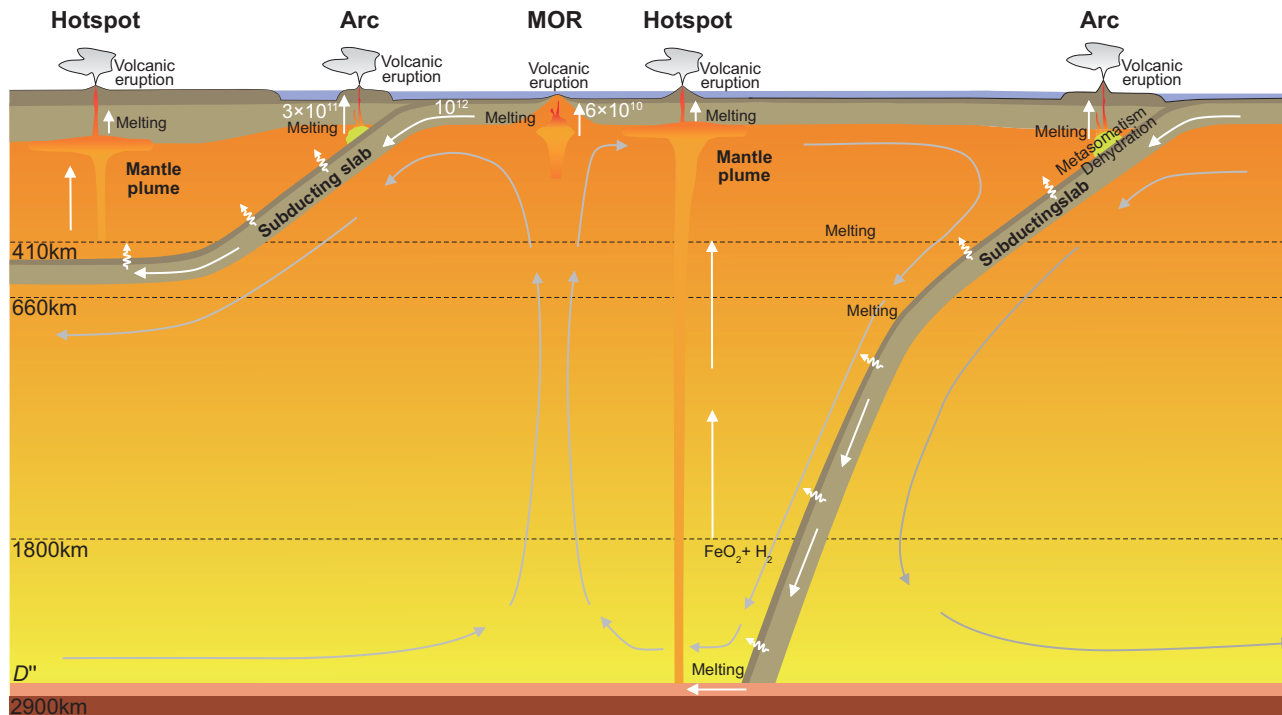


Figure 4. Earth's deep water cycle (delineated in white arrows). Plate subduction and volcanic eruptions (at subduction zones, mid-ocean ridges and hotspots) are the predominant mechanisms of ingassing and outgassing of water, respectively. The numbers indicate water fluxes in kg/yr. About one-third of water in subducted slabs is recycled at subduction zones through dehydration and melting. The other two-thirds arrive at >100 km depths and may replenish the source regions of OIBs, MORBs and continental basalts. Some slabs may become stagnant near the 660 km discontinuity and lose water to the transition zone and the overlying mantle. Some other slabs can subduct to the lower mantle, and the water they carry may be partly converted to H_2 beyond 1800 km depth. Mantle convection is shown in grey arrows. MOR, mid-oceanic ridge.

FROM EARLY EARTH TO THE PRESENT

The above discussion concentrates on the conditions and processes in the modern Earth, in which plate tectonics has operated at least since the Phanerozoic. The early Earth was much different. It was once believed that the Moon-forming giant impact ~ 4.5 Gyr ago deprived the Earth almost completely of its primordial water, forming dry terrestrial and lunar magma oceans, and that most water was added to the Earth during the 'later veneer' period by asteroids and comets [106]. However, there is growing evidence indicating that water loss during the giant impact was incomplete (especially if water oceans had not formed before the impact) and that the Earth had already developed water oceans by 4.4 Gyr ago [107–109]. Whether the shallow part of the terrestrial magma ocean was oxidized or reduced, water vapor was always a major component in the early atmosphere, and exchange of water between the magma ocean and the atmosphere was intensive [110,111]. Some water was likely lost to space at an early stage, but this process did not last long [112] as the geomagnetic field was established. Because much more water can be dissolved in melt than in minerals, crystallization would expel water to the atmosphere, whereas melting would resorb water into the mantle [16,113], in contrast with the modern Earth in which melting leads to dehydration of the mantle instead.

After the solidification of the magma ocean and condensation of water oceans, water vapor, alongside other greenhouse gases (e.g. CO_2 , CH_4 and NH_3), probably prevented the water oceans from being frozen by low solar luminosity [114,115]. In the traditional 'mantle degassing' (one-way process) model, the more primitive Hadean or Archean mantle should be more hydrous than the present mantle. However, even in the absence of plate tectonics, water could still be recycled to the mantle through other mechanisms, such as crustal delamination [116]. Furthermore, there are few geological records that suggest any major change in sea level, at least since the Phanerozoic. Therefore, a balance between water influx and outflux, and hence a balance for water storage between the surface and internal reservoirs, were probably established early in the Earth's history [16]. Water in the early Earth is believed to have played a critical role in initiating plate tectonics [21], perhaps some 3.0 Gyr ago [117]. Ever since then, the deep water cycle has been intimately coupled with plate tectonics, but it should have taken some time for plate tectonics to fully evolve to the modern style as observed today.

INFLUENCES OF WATER STORAGE AND CYCLING

The Earth's deep water cycle is more than simply a passive consequence of plate tectonics. As mentioned above, the initiation of subduction was probably promoted by lubrication by water [21]. The global workings of the modern Earth's interior are still being profoundly impacted by the storage and cycling of water [18,19].

Effect on rheological strength of minerals

Water dissolved in NAMs reduces their rheological strength (Fig. 5), referred to as the hydrolytic weakening effect [122], although there is debate over the magnitude of this effect [23,119,120,123]. Mantle convection and plate motion are generally believed to be significantly influenced by this effect, and the boundary between the asthenosphere and the lithosphere may simply reflect a viscosity contrast caused by different water contents [16,22,24,124]. The base of the cratonic mantle lithosphere may be hydrated by hydrous liquid phases derived from the subducting oceanic slab, leading to its weakening and thinning [41,46,125,126]. A related phenomenon is the pressure-dependent effect of water on the olivine fabrics and, consequently, on the seismic anisotropy of the upper mantle [124,127].

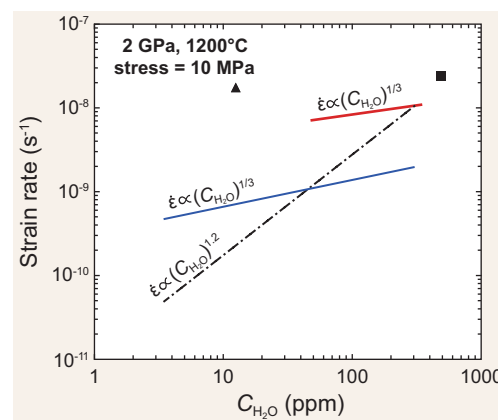


Figure 5. The increase of strain rate with water content in olivine (pure forsterite or Fo_{90}) based on different experimental studies using single crystal (red line: [118]; blue line: [119]; triangle: [120]) or polycrystalline (black dashed line: [121]; square: [24]) olivine, normalized to 2 GPa, 1200°C and a differential stress of 10 MPa.

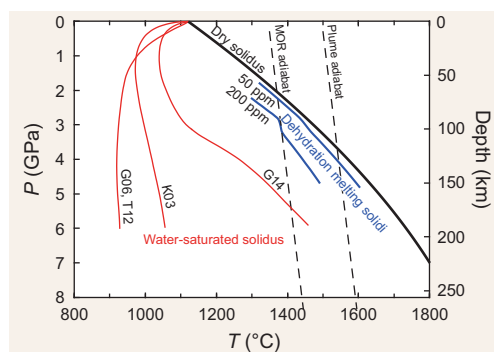


Figure 6. Effect of water on depressing the solidus (melting temperature) of mantle peridotite. Under water-undersaturated conditions, corresponding to mid-ocean ridges and mantle plumes (with their adiabatic geotherms shown in dashed lines), melting temperature decreases with increasing water content in the mantle (blue curves) [129,135]. There is huge disparity with water-saturated solidus (red curves), corresponding to subduction zone setting (K03: [131]; G06: [132]; T12: [133]; G14: [134]).

Effect on melting and other phase transitions

As a highly incompatible component, water dissolves more easily in silicate melts relative to minerals, thereby lowering the solidus of rocks and enhancing melting [27,128,129]. The effect of water on melting is the most obvious at subduction zones, such as flush melting of the oceanic crust and dehydration melting of the metasomatic mantle domains. Although volcanism at mid-ocean ridges is caused by decompression and that at hotspots is associated with thermal anomalies, in both cases water in mantle minerals increases the onset depth and degree of melting [14,130]. The effect of water on the solidus of peridotite at low water activity is relatively well constrained [129], but there are huge discrepancies between different experimental studies on water-saturated systems [131–134], as illustrated in Fig. 6.

Different zones of the mantle have contrasting water storage capacities. When mantle rocks migrate from a zone with high water storage capacity to another zone with low water storage capacity, the excessive water that cannot be accommodated in the mineral crystal structure induces partial melting [136]. This could occur at the lithosphere–asthenosphere boundary [137], at the base of the upper mantle [103], and at the base of the transition zone [95].

Magmatic evolution is also influenced by water, such as lowering the density and crystallization temperature of hydrous melts and altering the crystallization sequence [138–140]. Water also affects

mineral phase transition, thereby thickening seismic discontinuities [141–143].

Effects on elastic properties of minerals and seismic velocity

Water has a disproportionately large effect on the elastic properties and density of minerals, and hence on seismic velocities (V_P and V_S) and V_P/V_S ratio [144–147], which is probably due to the formation of cation vacancies [148]. A number of velocity anomalies in the upper mantle and in the transition zone cannot be explained by lateral temperature variation alone, and are suggested to be associated with the effect of water (e.g. [149–152]). Based on experimental and computational data for olivine polymorphs, the most abundant minerals in the mantle until the 660 km discontinuity, modeling results suggest that water could cause up to a 0.7% reduction in the velocity of the upper mantle and up to a 4.7% reduction in the transition zone [145] (Fig. 7). In the transition zone, the addition of water has a greater effect on the sound velocities of wadsleyite than for ringwoodite.

Effect on electrical conductivity of minerals and melts

Compared to seismic velocity, electrical conductivity is even more sensitive to the presence of water [153]. This is the case with both minerals and silicate melts [154–156]. The electrical conductivity of olivine is enhanced by an order of magnitude by several hundred ppm water [68,157],

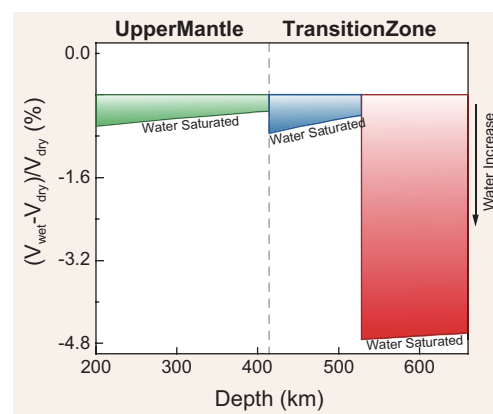


Figure 7. Effect of water on the seismic velocity (V) of the upper mantle and transition zone, based on experimental results for olivine polymorphs and a pyrolite model. The shaded regions are for water content ranging from nil to the water storage capacity of olivine polymorphs. The effects on P- and S-waves are similar [145] and are therefore not distinguished.

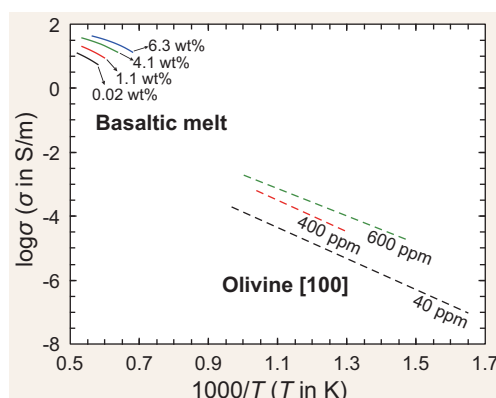


Figure 8. Effect of water on electrical conductivity of olivine [100] at 1 GPa and that of basaltic melt at 2 GPa. Based on experimental data in Yang [157] and Ni *et al.* [158].

and that of basaltic melt is enhanced by an order of magnitude by ~6 wt% water [158,159] (Fig. 8). However, the mechanisms of hydration effects are totally different. For minerals, it involves the transport of protons [154], but for silicate melts it is caused by enhanced mobility of cations associated with a viscosity decrease [155,160], as well as the participation of OH as charge carrier [161,162]. The effects of water on electrical conductivity and on seismic velocity can be used for remote-sensing of water distribution and hydrous melting in the Earth's interior by magnetotellurics and seismology [65,153,158,163].

Properties of hydrous phases

The above discussion deals with several prominent hydration effects on NAMs and silicate melts. It is equally important to know the physicochemical properties of innate hydrous phases, namely aqueous solutions and hydrous minerals, particularly their density, elastic properties [147,164–167] and electrical conductivity [159,168]. Such information is crucial for correct interpretations of seismological and magnetotelluric data and for the identification of water-rich zones in the Earth's interior. Furthermore, the breakdown of hydrous minerals during subduction causes the development of brittle fractures [169], which may be an important mechanism for intermediate- to deep-focus earthquakes [170–172].

OUTLOOK

While research progress over the past three decades has roughly described the distribution (Fig. 1), cycling (Fig. 4) and impact (Figs 5–8) of water in the Earth's interior, the following big questions still need to be answered.

- (1) How hydrous are the mantle transition zone and the lower mantle? How are their water contents influenced by whole-mantle convection over geological time?
- (2) Where are the solidi of basalt and peridotite under water-saturated conditions? How common is partial melting of the subducting oceanic crust at different depths?
- (3) What are the *P-T* conditions for the formation of supercritical fluids? How important is the role played by supercritical fluids at subduction zones?
- (4) What are the major carriers of water in subducting slabs at various depths? How do slabs exchange water with the mantle at different depths? How is the slab signal passed to OIBs and continental basalts?
- (5) How abundant are H₂ and other reduced hydrogen species in the deep mantle and the core?
- (6) How significant is the effect of water on mantle rheology and on the elastic and electrical properties of the lower mantle phases?
- (7) Does melting really occur at the lithosphere–asthenosphere, upper mantle–transition zone and transition zone–lower mantle boundaries due to contrasting water storage capacity? What is the influence of melting on the deep water cycle?
- (8) How much of Earth's water is primordial (i.e. has survived the giant impact)?
- (9) How have water distribution and cycling evolved from the early Earth to the present?

To resolve these critical issues around the deep water cycle, an integrated approach and concerted efforts are required from geochemical, geophysical and geodynamic studies. Research progress in these fields will greatly advance our understanding of the working mechanisms of the Earth's interior and their consequences on surface environments.

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