

INVITED REVIEW**Origin of Earth's oceans: An assessment of the total amount, history and supply of water**

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The presence of water on Earth has played important roles in shaping the solid regions of the planet as well as in the origin and evolution of life. This paper addresses three fundamental aspects of Earth's water; (1) the quantity of water on the surface and in the interior that Earth possesses, (2) the length of time that surface oceans have been present, and (3) the mechanism(s) by which this water was supplied or generated. From geochemical and geophysical analysis, and high-pressure experimental works, the water content in the Earth's mantle can be estimated to be from one to ten times the present ocean mass. Although it is difficult to estimate the water content in the Earth's core, recent high-pressure experimental work indicates copious amounts of hydrogen in the core. From geological and geochemical evidence, the Earth's surface oceans appear to have existed since very early in the Earth's history, perhaps even since the Earth's formation. However, changes in the ocean volume throughout the Earth's history have not been well determined. Several possible water sources and supply mechanisms have been proposed, in association with theories regarding planet formation in our solar system. Since there are several uncertainties concerning the process of planet formation, the origin of the Earth's water is still in question.

Keywords: origin of water, age of oceans, water in Earth, planet formation, snow line

INTRODUCTION

Our Earth is often referred to as an "aqua planet," due to the large quantity of water on its surface (71% of the Earth's surface is covered by oceans) compared to the other terrestrial planets in our solar system, such as Mercury, Venus and Mars. However, the mass of the Earth's oceans ($M_{\text{oce}} = 1.4 \times 10^{21}$ kg) is only 0.023 wt% of the planet's total mass ($M_{\text{E}} = 6.0 \times 10^{24}$ kg) (see Fig. 1). Even if the water in the Earth's interior (the mantle and core) is taken into account, the mass fraction of water does not exceed 2 wt% of the total planetary mass. In contrast, Uranus and Neptune, the outermost planets in the solar system, are composed primarily of H₂O (60–70 wt%) (e.g., Guillot, 2005). Therefore, Earth is not truly an aqua planet from the viewpoint of its H₂O content, and strictly speaking Uranus and Neptune are not aqua planets either, because their abundant H₂O is not in the form of liquid, but ice.

Water molecules (H₂O) are expected to be abundant in our solar system, since hydrogen is the most abundant element in the universe and oxygen is the third most abun-

dant element in the solar system (Anders and Ebihara, 1982). The second most abundant element, helium, is chemically inert and does not normally form molecules. In the protoplanetary disk from which our solar system planets formed, there were numerous H₂O molecules, likely amounting to two to three times the mass of the rock and iron that were the main building blocks of the terrestrial planets. Since H₂O molecules condense into ice beyond the Jovian planet region, it is a natural consequence that Neptune and Uranus were formed mainly from these ices. If the C/O ratio in an extrasolar system is more than unity, oxygen atoms are likely to combine with carbon atoms to form CO, and so H₂O is not produced. However, since the C/O ratios in most extrasolar systems are less than unity, as confirmed by observations of various stars (Petigura and Marcy, 2011), H₂O could be as abundant in extrasolar systems as in our solar system.

The distance from the central star (or from the sun in our solar system) is the most important factor determining the stability of liquid water on a planetary surface (e.g., Kasting *et al.*, 1993). If a planet orbits close to a star, all liquid water will be vaporized due to the runaway greenhouse effect of water vapor. A planet with oceans has an upper limit of planetary radiation (Kasting, 1988; Nakajima *et al.*, 1992; Kodama *et al.*, 2015). If a planet receives a solar energy flux above this upper limit,

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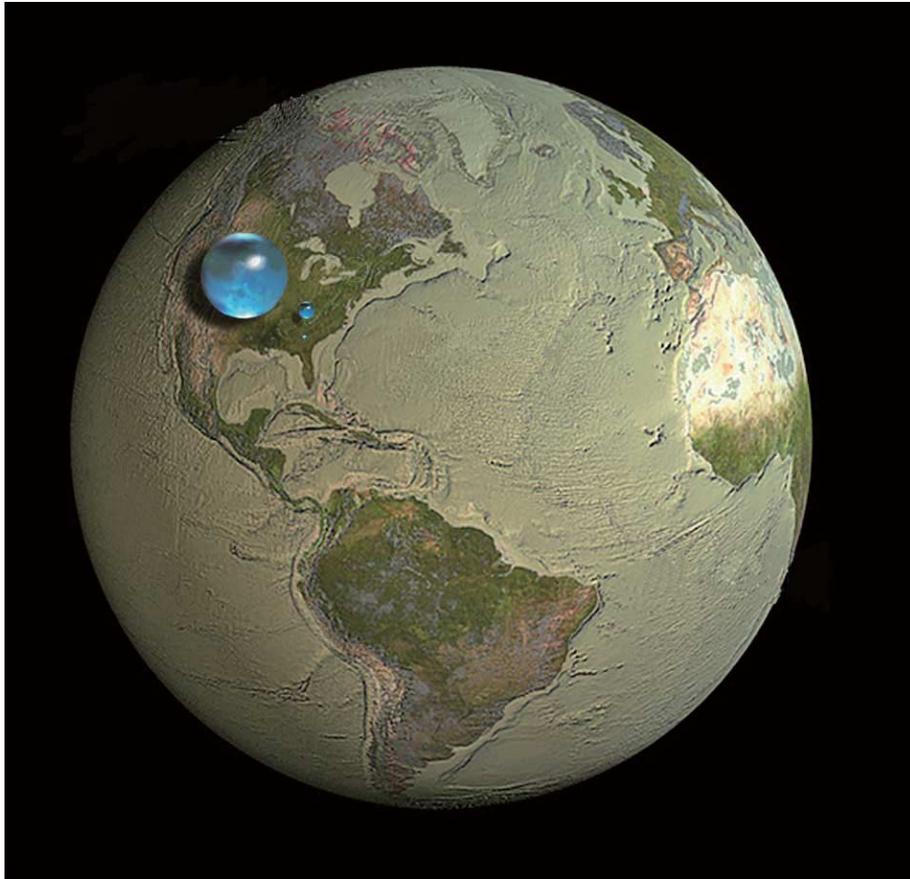


Fig. 1. The amount of water on Earth compared with the overall globe. (Note: two of the three droplets are quite small and may be difficult to see.) The largest droplet represents the volume of the Earth's oceans, the second largest droplet represents the total volume of water other than that in the oceans (such as in rivers, lakes, ground water, water vapor and the water in living organisms), and the smallest droplet represents the volume of water that humans can readily utilize. From Howard Perlman, USGS; globe illustration by Jack Cook, Woods Hole Oceanographic Institution; © Adam Nieman.

all water is vaporized. Conversely, a planet far from its star will hold only frozen water. The amount of atmospheric greenhouse gases is also important in determining the stability of liquid water. As an example, if Earth had no greenhouse gases (that is, no CO_2 or water vapor), its surface temperature could be as low as -15°C , and therefore it would be fully covered with ice. The adequate distance of Earth from the sun and a suitable amount of greenhouse gases in the Earth's atmosphere have made this planet habitable.

The water on Earth also plays many important roles in the solid regions of the planet. In plate tectonics, water acts a lubricant (e.g., Regenauer-Lieb *et al.*, 2001), and water also promotes long-term climate stability through the carbon cycle between the atmosphere and the planet (Walker, 1982; Tajika and Matsui, 1992). If, for example, Earth had ten times its present volume of oceanic water, there would be no dry continents and the Earth's environment would be quite different (Maruyama

et al., 2013). Therefore, an adequate amount of liquid water on the Earth's surface is also important in terms of forming and preserving the present Earth's surface environment.

Liquid water is one of the most important compounds required to support life (at least terrestrial life as we now know it), and many believe that liquid water played a significant role in the generation of living organisms on the planet. Indeed, H_2O molecule has many unique characteristics. Hydrogen bonding between molecules gives water its relatively high melting and boiling temperatures compared to other compounds with comparable molecular weights (Fig. 2). For this reason, liquid water is stable up to a reasonably high temperature, and so chemical reactions in aqueous solutions can potentially proceed rapidly, which has been advantageous with regard to the birth and evolution of life. The unique properties and high abundance of H_2O molecules in the universe suggest that extra-terrestrial life will also be water-based.

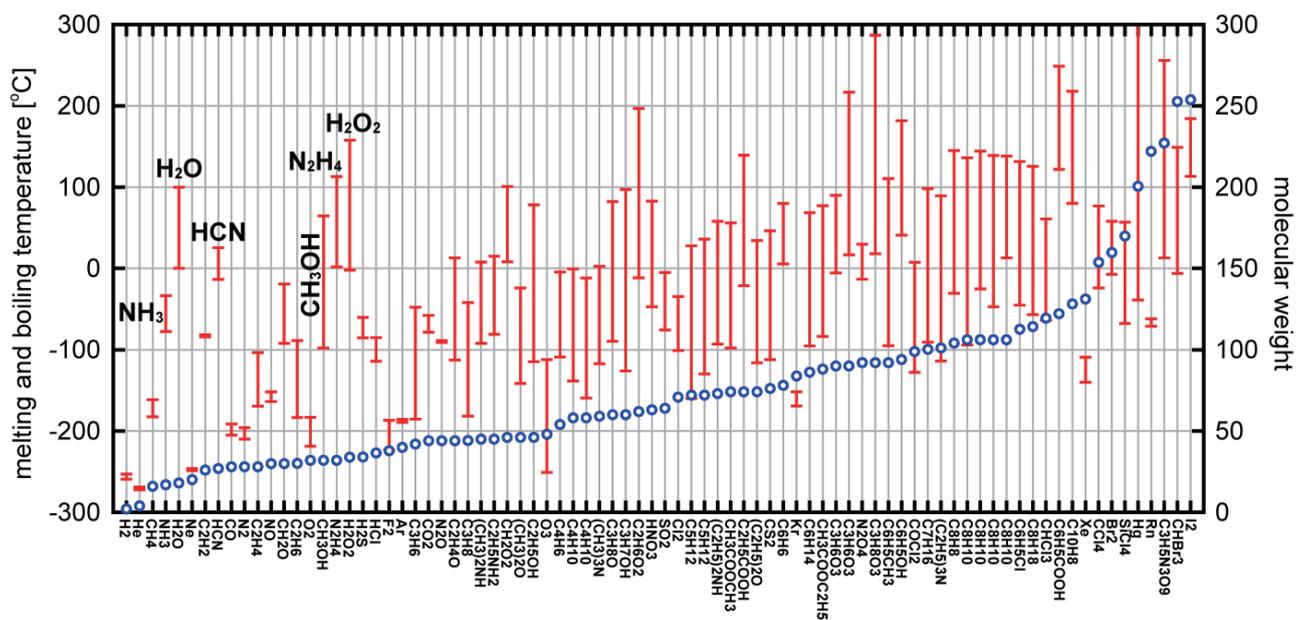


Fig. 2. Melting and boiling temperatures at 1 atm (lower and upper ends of red bars) and molecular weights (blue circles) of various compounds. Data are taken from Perry's Chemical Engineers' Handbook (Green and Perry, 2008), and Abe (2009).

Herein, three fundamental aspects regarding water on Earth are discussed. These are the actual quantity of water on the planet, including that in the mantle and core, the time length that surface oceans have been present, and the mechanism by which the planet acquired its present water.

EARTH'S WATER BUDGET

Surface water

The amount of water in the oceans on the Earth's surface (M_{occ}) has been determined with reasonable precision, and is reported to be 1.37×10^{21} kg. There are other water reservoirs on or around Earth, such as ice, groundwater, lakes, rivers, soils, sedimentary rocks, crust and the atmosphere, and the total mass of water in these reservoirs is estimated to approximately 5×10^{20} kg (Mottl *et al.*, 2007), a value that is about one half of M_{occ} .

Water in the mantle

The Earth's mantle could potentially represent a huge reservoir of water because of its large mass (4.0×10^{24} kg or 67 wt% of the Earth's mass). If the entire mantle contains on average 0.1 wt% water, this equates to 4.0×10^{21} kg of water, corresponding to 3 M_{occ} . Therefore, determining the water content in the mantle is vital in terms of assessing the overall water budget of the planet. However, precise and direct measurement of the water content in the mantle is quite difficult because we cannot access the mantle directly. Even the deepest hole drilled

to date (the Kola Superdeep Borehole in Russia) reached a depth of only 12 km (Kremenetsky and Ovchinnikov, 1986), and thus did not exit the Earth's crust. Nevertheless, we can infer the water content in the mantle by means of the extensive analysis of mantle-derived rock samples, geophysical probing methods such as electrical conductivity assessments of the mantle, and high-pressure experiments of hydrous minerals. Table 1 summarizes the estimated water content in the Earth's mantle determined by these methods.

Studies of water and trace elements in mid-ocean ridge basalts (MORBs), which are formed by partial melting of the upper mantle, indicate that the upper mantle contains between 50 and 200 ppm H₂O (Michael, 1988; Dixon *et al.*, 2002; Hirschmann, 2006). High-pressure experiments of olivine, the major component of the upper mantle, have shown that the water capacity of olivine increases with pressure, approaching 0.4 wt% (=4000 ppm by weight) at the lowermost regions of the upper mantle (410 km) (Bell *et al.*, 2003; Koga *et al.*, 2003). Since this measured value is not the actual water content in the upper mantle, but rather represents the holding capacity, the water content in the upper mantle estimated from MORB samples shows that the upper mantle is not fully saturated with water.

The electrical conductivity of the Earth's upper mantle also shows that the upper mantle is relatively dry. It is known that the electrical conductivity of mantle minerals is strongly correlated with their water content. Therefore, measuring the electrical conductivity of the Earth's

Table 1. Estimated water contents in the Earth's mantle

Mantle	Mass (10^{21} kg)	Natural samples	Electrical conductivity	High-pressure experiments	Water mass (M_{occ})
Upper mantle	615	50–200 ppm ^[1]	<0.09 wt% ^[4]	<0.4 wt% ^[6]	0.02–2
Transition zone	415	~1 wt% ^[2]	~0.1 wt% ^[5]	~2 wt% ^[7]	0.3–5
Lower mantle	2955	300–1000 ppm ^{2[3]}	—	~0.2 wt% ^[8]	0.6–4

Data from [1] Hirschmann (2006), [2] Pearson *et al.* (2014), [3] Dixon *et al.* (1997, 2002), Hauri (2002), [4] Wang *et al.* (2008), [5] Yoshino *et al.* (2008), Huang *et al.* (2005), [6] Bell *et al.* (2003), Koga *et al.* (2003), [7] wadsleyite: Inoue *et al.* (1995, 1998), ringwoodite: Kohlstedt *et al.* (1996), [8] Murakami *et al.* (2002), Litasov *et al.* (2003).

mantle can provide information concerning the water concentration. The electrical conductivity has been ascertained based on electromagnetic induction theory by measuring magnetic and electric fields both on the ground and using artificial satellites (Olsen, 1999; Kuvshinov and Olsen, 2006; Püthe and Kuvshinov, 2013). Combining the observed data with the experimentally determined electrical conductivity of high-pressure hydrous minerals, the water contents have been estimated at 10–900 ppm in the upper mantle (Wang *et al.*, 2008), and at <0.1 wt% (Yoshino *et al.*, 2008) and at 0.1–0.2 wt% (Huang *et al.*, 2005) in the transition zone. There is no reliable data concerning the lower mantle.

The transition zone, ranging from 410 to 660 km, is thought to be a potentially huge water reservoir. Wadsleyite and ringwoodite are high-pressure polymorphs of olivine, and dominate the transition zone. High-pressure experiments on the solubility of H₂O in these minerals show that wadsleyite and ringwoodite can contain 3.3 wt% (Inoue *et al.*, 1995, 1998) and 2.2 wt% H₂O (Kohlstedt *et al.*, 1996), respectively. Since about 60 wt% of the transition zone is composed of these minerals, the transition zone could potentially contain a mass of water equal to 5 M_{occ} . However, the water content estimated by electrical conductivity measurements of the transition zone (approximately 0.1 wt%) does not support a water saturated transition zone (Yoshino *et al.*, 2008; Huang *et al.*, 2005).

Recently, Pearson *et al.* (2014) found a hydrous ringwoodite inclusion in a diamond sourced from Juína, Brazil. This was the first discovery of ringwoodite in natural samples on Earth, although this mineral has been identified in meteorites and synthesized in laboratories. The water-rich nature of this inclusion was direct evidence for a wet transition zone, at least locally. Pearson *et al.* (2014) estimated that the transition zone contains approximately 1 wt% water.

Geochemical studies of oceanic island basalts (OIBs) suggest that the water content of the OIB source ranges from 300 to 1000 ppm (Dixon *et al.*, 1997, 2002; Hauri, 2002). If OIBs come from the lower mantle, this region could also represent a significant water reservoir. High-pressure experiments of lower mantle minerals support

the prediction of a large amount of water in the lower mantle. Murakami *et al.* (2002) reported that the major minerals of the lower mantle could hold water up to 0.2 wt% for Mg-perovskite, 0.4 wt% for Ca-perovskite, and 0.2 wt% for magnesiowüstite.

Thus, although an exact determination of the water content in the entire Earth's mantle is difficult, the value evidently is in the range of 1–10 M_{occ} (see Table 1).

Hydrogen in the core

Experimental studies of hydrogen partitioning between the hydrous silicate melt and molten iron show that more than 95% of H₂O reacts with Fe to form FeH_X at 7.5 GPa (Okuchi, 1997). Therefore if Earth had held water during the magma ocean stage, a significant fraction of the hydrogen in the water would have been incorporated into the Earth's core.

Seismic velocity data shows that the density of the Earth's liquid outer core is 5–10 wt% less than that of pure iron (Birch, 1952; Dubrovinsky *et al.*, 2000; Dewaele *et al.*, 2006). To account for this density deficit, the core must contain a considerable amount of light elements, such as Si, O, S, C and/or H (e.g., Poirier, 1994; Hirose *et al.*, 2013). In the extreme case in which H is considered as the only light element in the core, the density deficit could be entirely reconciled by assuming 0.5–1.0 wt% H in the form of FeH_X (X = 0.28–0.56) (Narygina *et al.*, 2011). Since the mass of the outer core is 1.9×10^{24} kg, this amount of H corresponds to H in the water of 60–120 M_{occ} .

Recently, Nomura *et al.* (2014) showed experimentally that the solidus temperature of pyrolite (a theoretical rock representing the mantle) is 3570 K at the core-mantle boundary (CMB), a value that is about 400 K lower than previously thought. Since a lower temperature at the CMB also implies a lower temperature at the core, the melting temperature of the outer core must be greatly depressed in order for the inner part of the core to solidify. Since such a large depression is impossible without the presence of hydrogen in the core (Alfè *et al.*, 2007; Sakamaki *et al.*, 2009), Nomura *et al.* (2014) concluded that the outer core must contain high concentration of hydrogen corresponding to an amount of water equal to



Fig. 3. Pillow lava basalt in Isua, Greenland, which erupted under water at 3.8 Ga. The grey-green portion is the core of the pillow and is mantled by a dark green portion, which in turn is rimmed by pale-colored chilled margins, together with the matrix. The scale is given by a hammer at the top of the photo. Courtesy of Museum of Evolving Earth, Tokyo Institute of Technology.

80 M_{oce} . Therefore, the core is potentially a huge reservoir of water (up to approximately 100 M_{oce}). However, since we have no direct samples from the Earth's core, we cannot confirm the hydrogen content in the core.

HOW LONG HAVE THE EARTH'S OCEANS EXISTED?

Geological and geochemical constraints

At present, it is thought that the oceans have existed since the very early stage of the Earth's history. Direct evidence for the existence of an ancient ocean is provided by pillow lava formed throughout the Earth's history and located in various locations around the planet. This lava is characterized by pillow-shaped masses, as shown in Fig. 3, and is formed when hot lava flows into water and cools rapidly. The oldest pillow lavas were found in the Isua Supracrustal Belt, southwestern Greenland, and were determined to have formed at 3.7–3.8 Ga (Appel *et al.*, 1998; Maruyama and Komiya, 2011). Therefore, the Earth's oceans must have existed at 3.8 Ga.

The oldest rock sampled to date comes from Acasta Gneiss, northwestern Canada, and is dated to 4.0 Ga (Bowring *et al.*, 1989; Bowring and Williams, 1999), thus there are no geological rock records on Earth before 4.0 Ga, and the first approximately 500 Ma of the Earth's history remains poorly understood. However, it is possible to locate zircon (ZrSiO_4) that can be dated before 4.0

Ga. Zircon is a mineral that is highly resistant to erosion, weathering and metamorphism. During the Hadean era which ranged from 4.5 Ga (the Earth's formation) to 4.0 Ga, all Earth's rock records prior to 4.0 Ga has been missing and/or has been destroyed likely by early intense meteor bombardment, but zircon grains are thought to have survived this era (e.g., Marchi *et al.*, 2014). Hadean zircon grains have high oxygen isotope ($\delta^{18}\text{O}$) values (Wilde *et al.*, 2001; Mojzsis *et al.*, 2001; Valley *et al.*, 2014), indicating that the Earth's oceans existed during the Hadean era. High $\delta^{18}\text{O}$ values of zircon grains compared with the mantle are produced by low-temperature interactions between rocks and liquid water. Zircon grains with the ages of 3.91 to 4.28 Ga have high $\delta^{18}\text{O}$ values ranging from 5.4 ± 0.6 to $15.0 \pm 0.4\%$, suggesting interactions between the continental crust and oceans (Mojzsis *et al.*, 2001). Again, this presents evidence for the existence of Earth's oceans during the Hadean era.

The early formation of the Earth's atmosphere deduced by noble gas geochemistry (Hamano and Ozima, 1978; Staudacher and Allègre, 1982) is also consistent with the presence of oceans on early Earth. As an example, Hamano and Ozima (1978) estimated the timing and degassing rate of Ar from the Earth's interior, and showed that more than 80% of the internal Ar must have degassed to the surface during the Hadean era to explain the present low $^{40}\text{Ar}/^{36}\text{Ar}$ ratio in the air (≈ 295.5) compared to the

extremely high $^{40}\text{Ar}/^{36}\text{Ar}$ ratios in MORB samples ($>30,000$). The degassing of Ar likely also involves the degassing of other volatiles, such as CO_2 and H_2O .

Both the geological and geochemical evidence discussed above show that the Earth's oceans have existed since the very early stages of Earth's history. Moreover, water in lunar samples, such as volcanic glasses (Saal *et al.*, 2008; Hauri *et al.*, 2011), apatite crystals in lunar volcanic rocks (McCubbin *et al.*, 2010; Boyce *et al.*, 2010) and plagioclase crystals in lunar highland rocks (Hui *et al.*, 2013), has been discovered recently. Especially, the presence of water in plagioclase strongly supports the supply of water on Earth and Moon prior to their formation (i.e., at 4.5 Ga), because lunar plagioclase was crystallized from lunar magma ocean related to lunar formation just after the giant impact. Therefore, Hui *et al.* (2013) concluded that the Moon must have contained a significant amount of water at the time at which it was formed. They also estimated that the water content in the lunar magma ocean could have been as high as 320 ppm, a value similar to the concentration of water in the upper mantle of present Earth, although this high value of water concentration might be overestimated if the recent calibration of the FTIR work is applied (Losq *et al.*, 2015). Geophysical data concerning the moon's electrical conductivity and tidal quality factor also support the existence of a wet lunar interior (Karato, 2013) containing as high water concentration (approximately 100 ppm) as the Earth's upper mantle. Therefore, water was presumably supplied to Earth as well as the Moon prior to their formation.

Ocean volume changes throughout the Earth's history

There is almost no doubt that the Earth's oceans have existed throughout the Earth's history. However, estimating the ocean volume in the past is much more difficult than simply confirming their presence. The volume of the ocean would have varied by means of the loss of hydrogen into outer space and/or the exchange of water between the Earth's interior and the oceans.

The escape rate of hydrogen into space from present-day Earth is estimated at approximately 3 kg/s (Hunten, 1982). If this rate was constant as far back as 4.5 Ga, the total loss of hydrogen would be 4×10^{17} kg, corresponding to 3.9×10^{18} kg of water or 0.2% of the present Earth's ocean mass. Therefore, the current escape rate of hydrogen has little effect on the ocean volume. This rate is controlled by the diffusion of the hydrogen carrier (H_2O in the present Earth's atmosphere) in the atmosphere. In the case of present-day Earth, the cold trap of water vapor (i.e., condensation of water vapor) results in very low concentrations of water vapor ($\sim 10^{-7}$) in the upper atmosphere (e.g., Goody, 1995). Therefore, the current escape rate of hydrogen is extremely low. In the case of very

high surface temperatures, such as on Venus, the cold trap vanishes and extreme hydrogen loss takes place. This phenomenon was responsible for water loss on the ancient Venus (Kasting *et al.*, 1993; Hamano *et al.*, 2013).

If the concentration of CH_4 in the ancient atmosphere was more than 10 times higher than that in present Earth, CH_4 would have replaced H_2O as the main hydrogen carrier, leading to a high hydrogen escape rate. Pope *et al.* (2012) reported that Archean oceans were depleted in deuterium ($\delta\text{D} = -25 \pm 5\text{‰}$) based on the analysis of serpentine from the approximately 3.8 Ga Isua Supracrustal Belt in western Greenland. Tomiyasu *et al.* (2013) also reported that Archean oceans depleted in deuterium ($\delta\text{D} = -24 \pm 5\text{‰}$) judging from the analysis of pillow basalts from the approximately 3.5 Ga Barberton Greenstone Belt in South Africa. Hydrogen escape into space increases the value of δD over time, since hydrogen is lighter and thus escapes more readily than deuterium (Hunten, 1973; Genda and Ikoma, 2008). Pope *et al.* (2012) concluded that the early Earth oceans were about 26% more voluminous than at present. High concentrations of CH_4 in the early Earth atmosphere would have been responsible for this significant loss of hydrogen. The D/H ratio of ancient oceans would be the key to tracing the history of changes to the ocean volume.

The exchange of water between the Earth's interior and the oceans would also change the ocean volume. Water is outgassed from the mantle via volcanism at mid-ocean ridges, ocean islands, arcs and back-arc basins. In addition, water is lost from the ocean at subduction zones via the subduction of slabs with water-bearing rocks such as sediments, altered oceanic crust and serpentinized lithospheric mantle. In subduction zones, the present ingassing water flux is estimated to be 9×10^{11} – 1.9×10^{12} kg/yr (Rea and Ruff, 1996; Javoy, 1998). Present outgassing water fluxes at mid-ocean ridges and arcs are estimated to be 2×10^{11} – 5×10^{11} kg and 1.9×10^{11} – 1.5×10^{12} kg/yr (Bounama *et al.*, 2001; Hilton *et al.*, 2002), respectively. Therefore, present ingassing and outgassing water fluxes are almost comparable. However, if this balance were to change, the ocean volume would also change significantly. As an example, if either outgassing or ingassing of water were to completely terminate, about 5 times the volume of the present oceans would be transferred during 4.5 Ga. Moreover, the past outgassing and ingassing water fluxes are more difficult to estimate than the present values. Therefore, the exchange of water between the Earth's interior and oceans must have played a significant role in varying the volume of the Earth's oceans over time.

SUPPLY OF WATER ON EARTH

How did the Earth's water originate? Where did the

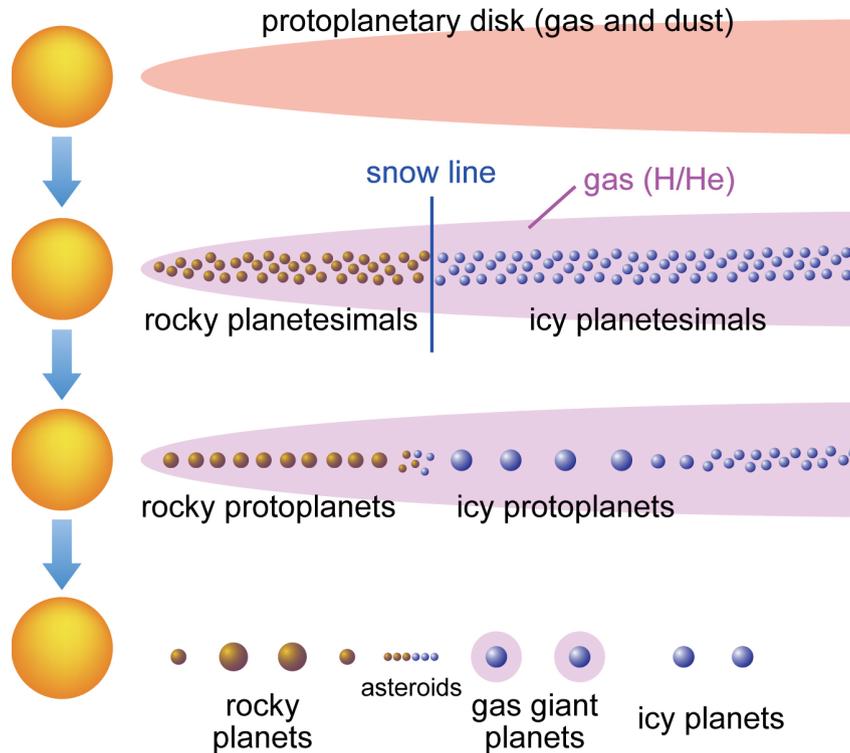


Fig. 4. Summary of planet formation in our solar system. A protoplanetary disk composed of gas and dust forms around the sun during star formation and planets are generated from this disk.

Earth's water come from? Here, three possible sources of water and supply mechanisms are reviewed. The process of water supply to Earth is closely related to the dynamics and chemistry of planet formation. First, the standard scenario of planet formation in our solar system is discussed, after which possible water sources and supply mechanisms are detailed.

Planet formation in our solar system

An outline of planet formation is provided in Fig. 4. Planets are formed in a protoplanetary disk around a star (otherwise known as a nebular disk, or simply nebula), composed of gas and dust. This disk is typically the by-product of star formation (e.g., Armitage, 2011). Terrestrial planets are made primarily from the dust component of the disk, and cores of Jovian planets are made from dust component (rock and ice), following which these cores gather the surrounding gas component (H_2 and He).

There are several stages involved in planet formation. The first stage is the formation of a large number of kilometer-sized bodies known as planetesimals by accretion of dust particles (Johansen *et al.*, 2007; Cuzzi *et al.*, 2008). Rocky planetesimals are formed inside the snow line (the boundary between condensation and vaporization of H_2O), and icy planetesimals are formed outside the snow line.

In the second stage, these planetesimals collide to produce protoplanets (e.g., Genda *et al.*, 2015a). Within the terrestrial planet region in our solar system (inside the snow line), a few tens of rocky Mars-sized protoplanets were formed (Wetherill, 1985; Kokubo and Ida, 1998, 2000; Kokubo *et al.*, 2006). Since solid materials were plentiful in the Jovian planet region (beyond the snow line) due to the presence of ice as well as rocky materials at large distances from the sun, a few huge icy protoplanets (often called cores) with masses several times those of Earth were formed (Tanaka and Ida, 1997; Kokubo and Ida, 2002; Kobayashi *et al.*, 2010). These huge protoplanets began to gravitationally attract the surrounding nebular gas in a runaway manner, eventually forming gas giant planets such as Jupiter and Saturn (Mizuno, 1980; Bodenheimer and Pollack, 1986; Pollack *et al.*, 1996; Ikoma *et al.*, 2000). Since the formation timescales of protoplanets beyond Saturn were much longer than the dissipation timescale of the nebular gas, these protoplanets did not capture a large amount of nebular gas. These icy protoplanets remain in the outer solar system forming Neptune and Uranus (Kokubo and Ida, 2002).

After the formation of Jupiter and Saturn, the final stage of terrestrial planet formation was characterized by collisions among rocky protoplanets (Chambers and

Wetherill, 1998; Agnor *et al.*, 1999; Kokubo and Genda, 2010; Genda *et al.*, 2012). These collisions are referred to as giant impacts. A giant impact (likely the last one) would be responsible for the formation of the Moon (Genda and Abe, 2003a; Canup, 2004; Ćuk and Stewart, 2012). In the terrestrial planet region, rocky planets such as Earth and Venus were formed during this stage. Because of the significant effects of the gravitational pulls of Jupiter and Saturn, terrestrial planets were not formed in the region between Mars and Jupiter, corresponding to the asteroid belt.

Planetesimals around Earth's orbit

If the building blocks of Earth (that is, planetesimals at approximately 1 AU) had contained small amounts of water, Earth would have originated as a wet planet. When a planet grows to lunar size (approximately 10^{23} kg), water will begin to degas from the planetesimals, and a significant steam atmosphere will form, followed by the formation of oceans (Matsui and Abe, 1986; Zahnle *et al.*, 1988). Therefore, Mars-sized protoplanets might have had surface oceans during terrestrial planet formation. Although giant impacts between these protoplanets were highly energetic events, significant amounts of water would have been able to survive these impacts (Genda and Abe, 2003b, 2005; Schlichting *et al.*, 2015).

The main question regarding this scenario is whether or not the planetesimals at approximately 1 AU contained water. According to the classical model of the protoplanetary disk, the temperature distribution in the disk is determined by the intensity of the solar radiation. In the case of our sun, the temperature of a body around 1 AU is estimated to have been 270 K (Hayashi, 1981). Since H_2O condenses to ice below 160–170 K at the gas pressure in a protoplanetary disk (approximately 1 Pa), the estimated temperature would have been too high to allow H_2O condensation. Therefore, planetesimals in the 1 AU region would have been dry. This disk model predicts that the snow line would have been located in the vicinity of the main asteroid belt, which is consistent with the observed water distribution of the main asteroid belt, in which C-type asteroids are distributed outside, and S-type asteroids inside (Gradie and Tedesco, 1982; Mothé-Diniz *et al.*, 2003).

Even if the snow line was located beyond 1 AU, there is the possibility that dry dust grains in the surrounding nebular gas could have absorbed water vapor on their surfaces (Stimpfl *et al.*, 2006), and so planetesimals made from these dust grains would contain small amounts of water. Izidoro *et al.* (2013) performed numerical simulations of terrestrial planet formation taking absorbed water into account, and showed that the contribution of absorbed water at approximately 1 AU was comparable to the water supplied by water-carrying asteroids beyond

the snow line.

Moreover, recent protoplanetary disk models suggest that the snow line moves with time, and so may have been temporarily located inside 1 AU (Chiang and Goldreich, 1997; Sasselov and Lecar, 2000; Oka *et al.*, 2011). Here, it is assumed that the numerous dust particles blocked the transmission of light from the sun, such that the temperature distribution was lower than predicted by the classical disk model. During planetesimal formation, there were presumably numerous dust particles in the protoplanetary disk. If this is correct, icy planetesimals such as comets were inevitably formed in the vicinity of 1 AU (Machida and Abe, 2010). However, this is inconsistent with the very small amount of water currently on Earth. Additionally, if dusts and/or pebbles that originated beyond the snow line migrate inward in the gaseous disk (e.g., Ciesla, 2009; Simon *et al.*, 2011; Guillot *et al.*, 2014), these water-carrying particles could contribute to the Earth's building blocks, and could affect Earth's water budget in some degree. Therefore, the absorption of water onto the surface of dust grains, the timing of planetesimal formation, the evolution of the snow line, and radial mixing of small particles in a gaseous disk are the important factors in understanding the water content of Earth's building blocks, and further detailed research is required.

External sources of water (asteroids and comets)

As noted the amount of water in Earth's oceans is tiny compared with the Earth's mass. Therefore, even if the main building blocks of the planet were completely dry, the small addition of water-carrying objects onto Earth is sufficient to explain the present Earth's oceans. As an example, since carbonaceous chondrites and comets have approximately 5 wt% and 80 wt% water, respectively, the accretion of these objects to provide only 1% of Earth's mass is sufficient to have contributed the present ocean mass.

In the above scenario, Earth receives a tiny amount of volatile-carrying material after it is fully formed. This is referred to as the late-veneer hypothesis. Originally, this hypothesis was proposed to explain the excessive concentration of highly siderophile elements (HSEs) such as Ru, Rh, Pd, Re, Os, Ir, Pt and Au in the Earth's mantle (e.g., O'Neill and Palme, 1998). Additionally, the relative abundance of HSEs in the Earth's mantle is similar to that in CI chondrites, which belong to the carbonaceous chondrites group and are highly oxidized and thus free of metallic iron (e.g., O'Neill and Palme, 1998). Therefore, if a tiny amount of metallic iron-free objects such as CI chondrites impinged on the planet following the formation of the Earth's core, the excessive abundance of HSEs in the mantle would be explained. Because CI chondrites are rich in volatiles such as water and organic compounds,

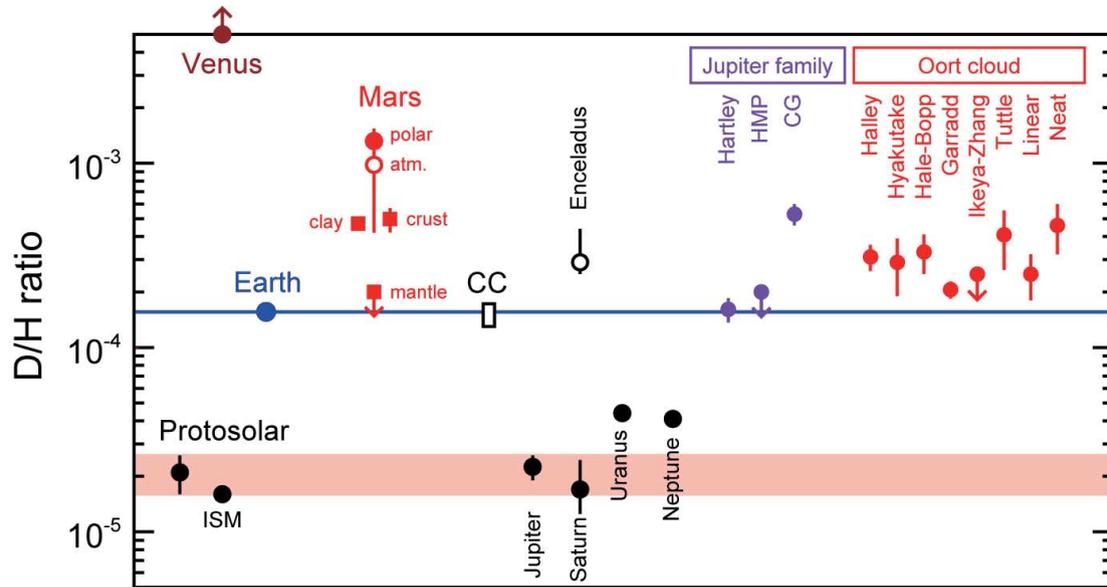


Fig. 5. D/H ratios in various objects in the solar system. All data are from Table 2. Legend: ISM = interstellar medium, CC = carbonaceous chondrites, HMP = Honda-Mrkos-Pajdušáková, CG = Churyumov-Gerasimenko.

the late veneer has also been considered a possible source of both the Earth’s water and atmosphere.

Several mechanisms by which water-carrying objects can land on Earth from outside the terrestrial planet region have been proposed to date. Due to the gravitational disturbance of the asteroid belt region by Jupiter, it has been proposed that a large fraction of asteroids is ejected, some of which collide with Earth (Morbidelli *et al.*, 2000; Raymond *et al.*, 2009), which is consistent with the extreme mass depletion of the present asteroid belt. The migrations of Uranus and Neptune also result in the scattering of icy planetesimals (that is, comets), and a number of these bodies have entered the terrestrial planet region and are considered to be responsible for the late heavy bombardment around 4 Ga (Gomes *et al.*, 2005) that would be recorded on lunar samples. It should be noted that the amount of water supplied to Earth by comets has likely been minor (Gomes *et al.*, 2005), although comets have significantly affected the noble gas budget on Earth due to their high noble gas concentration (Dauphas, 2003).

Recently, in order to explain the reason why Mars is so small compared to Earth and Venus, Walsh *et al.* (2011) proposed the new “Grand Tack” scenario. Here, Jupiter migrates inward to the present orbital location of Mars and then returns to its present position during the planet formation stage, resulting in significant scattering of asteroids and icy planetesimals. In this scenario, water equal to 5–10 M_{oce} could have been supplied on Earth (O’Brien *et al.*, 2014).

Another possible explanation for the low mass of Mars is that the planetesimal disk was originally truncated in

the vicinity of Mars’ orbit, such that a small Mars was naturally formed (Hansen, 2009). A truncated disk would be expected if the protoplanetary disk was a dynamic environment experiencing turbulence (Papaloizou and Nelson, 2003; Jin *et al.*, 2008). Izidoro *et al.* (2014) carried out numerical simulations concerning terrestrial planets originating from a truncated disk and succeeded in making small terrestrial planets around 1.5 AU such as Mars. They also showed that Earth-sized planets in the vicinity of 1 AU would have received a sizeable quantity of water comparable to M_{oce} .

Nebular gas

If a planet is formed in a nebular gas, it will gravitationally attract the surrounding gas, generating a hydrogen-rich atmosphere (Hayashi *et al.*, 1979; Mizuno *et al.*, 1980; Pollack *et al.*, 1996). When a protoplanet grows to lunar size (approximately 10^{23} kg) through the successive accretion of planetesimals, it begins to attract the surrounding nebular gas (Ikoma and Genda, 2006). If oxygen had been supplied from oxides in the Earth’s interior to the hydrogen atmosphere, water molecules would have been formed on the planetary surface (Sasaki, 1990). The amount of water resulting from this process would depend on the oxides that were available in Earth. For example, iron oxides such as FeO and Fe₃O₄ can react with atmospheric hydrogen to produce a mass of water comparable to the mass of hydrogen that the planet attracts (Ikoma and Genda, 2006). Therefore, if a planet attracts a large quantity of hydrogen and a magma ocean is formed that can effectively react with the atmospheric

Table 2. D/H ratios in various objects in the solar system

Object	D/H ($\times 10^{-4}$)	Reference
Protosolar	0.21 ± 0.05	Geiss and Gloeckler (1998)
Interstellar medium	0.16 ± 0.01	Linsky <i>et al.</i> (2006)
Earth (SMOW)	1.56	De Wit <i>et al.</i> (1980)
Venus	160 ± 20	Donahue <i>et al.</i> (1982)
Mars		
atmosphere	4.2–15.4	Fisher (2007)
estimated polar ice	~12.5	Villanueva <i>et al.</i> (2015)
clay mineral	4.7 ± 0.3	Mahaffy <i>et al.</i> (2015)
crust	4–6	Boctor <i>et al.</i> (2003), Greenwood <i>et al.</i> (2008)
mantle	<2	Usui <i>et al.</i> (2012)
Carbonaceous chondrites	1.3–1.7	Robert (2003)
Jupiter	0.225 ± 0.035	Lellouch <i>et al.</i> (2001)
Saturn	$0.170 (+0.075/-0.045)$	Lellouch <i>et al.</i> (2001)
Enceladus	$2.9 (+1.5/-0.4)$	Waite <i>et al.</i> (2009)
Uranus	0.44 ± 0.04	Feuchtgruber <i>et al.</i> (2013)
Neptune	0.41 ± 0.04	Feuchtgruber <i>et al.</i> (2013)
Jupiter family		
103P/Hartley 2	1.61 ± 0.24	Hartogh <i>et al.</i> (2011)
45P/Honda-Mrkos-Pajdušáková	<2.0	Lis <i>et al.</i> (2013)
67P/Churyumov-Gerasimenko	5.3 ± 0.7	Altwegg <i>et al.</i> (2015)
Oort cloud		
1P/Halley	3.1 ± 0.5	Balsiger <i>et al.</i> (1995), Eberhardt <i>et al.</i> (1995)
C/1996 B2 Hyakutake	2.9 ± 1.0	Bockelée-Morvan <i>et al.</i> (1998)
C/1995 O1 Hale-Bopp	3.3 ± 0.8	Meier <i>et al.</i> (1998)
C/2009 P1 Garradd	2.06 ± 0.22	Bockelée-Morvan <i>et al.</i> (2012)
153P/Ikeya-Zhang	<2.5	Biver <i>et al.</i> (2006)
8P/Tuttle	4.09 ± 1.45	Villanueva <i>et al.</i> (2009)
C/2002 T7 Linear	2.5 ± 0.7	Hutsemékers <i>et al.</i> (2008)
C/2001 Q4 Neat	4.6 ± 1.4	Weaver <i>et al.</i> (2008)

hydrogen, a mass of water comparable to that of the present Earth's oceans would result. However, the generation of water via gravitationally attracted nebular atmosphere is inconsistent with some geochemical constraints observed in Earth (Genda and Ikoma, 2008), as discussed below.

D/H ratios in our solar system and other geochemical constraints

The deuterium/hydrogen (D/H) ratios in various planetary materials can give exceptional insights into the origin of Earth's water. Figure 5 and Table 2 summarize the D/H ratios for the Earth's oceans (SMOW or standard mean ocean water), and of various planetary materials, including the water sources discussed above, such as carbonaceous chondrites, comets and protosolar nebula. Unfortunately, little is known about the D/H ratios for

the Earth-forming planetesimals around 1 AU that could potentially have held water.

The D/H ratio for the Earth's oceans (SMOW) is 1.56×10^{-4} (de Wit *et al.*, 1980), a value that is similar to the D/H ratio for carbonaceous chondrites, which ranges from 1.3×10^{-4} to 1.7×10^{-4} in bulk samples (Robert, 2003). In contrast, the D/H ratios for comets are generally higher than that of SMOW. The long-period comets, which originate from the Oort cloud, all have values approximately twice that of SMOW (e.g., Drake and Righter, 2002). Recently, Hartogh *et al.* (2011) reported that the Jupiter family comet 103P/Hartley2 has a D/H value similar to that of Earth's oceans ($(1.61 \pm 0.24) \times 10^{-4}$) based on studies using the Herschel Space Observatory. Lis *et al.* (2013) reported that the upper limit of D/H for another Jupiter family comet, 45P/Honda-Mrkos-Pajdušáková, was 2.0×10^{-4} , suggesting that it also has an Earth's

ocean-like D/H. However, Altwegg *et al.* (2015) reported that the D/H ratio for the Jupiter family comet 67P/Churyumov-Gerasimenko ($(5.3 \pm 0.7) \times 10^{-4}$) is more than twice the SMOW value, based on observations made by the Rosetta spacecraft. Therefore, there seems to be a wide range of D/H values within the Jupiter family comets.

The atmosphere of Venus has an extremely high D/H ratio ($(1.6 \pm 0.2) \times 10^{-2}$) (Donahue *et al.*, 1982), more than 100 times as high as the SMOW value, as the result of the extreme loss of water from this planet (e.g., Chassefière *et al.*, 2012). The D/H ratio for the Martian atmosphere changes significantly with the season, ranging from 4.2×10^{-4} to 15.4×10^{-4} (Fisher, 2007), while the D/H ratio for polar ice (the main reservoir of H₂O on Mars) is estimated to be approximately 1.2×10^{-3} (Villanueva *et al.*, 2015), which is about 8 times the SMOW value. The D/H ratio for hydrated crust and/or ground ice is estimated to be 2–3 times the SMOW value from analysis of martian meteorites (Usui *et al.*, 2015). Although the D/H ratios at the Martian surface (the atmosphere, polar ice, clay minerals and crust) are higher than the SMOW value, Usui *et al.* (2012) reported that the D/H ratio for the Martian mantle is comparable to the SMOW value. Assuming that the D/H ratio for the Martian mantle did not change during 4.5 Ga, the loss of water from Mars would increase the D/H ratio at the Martian surface (e.g., Kurokawa *et al.*, 2014), which is consistent with the recent in situ D/H analysis of ancient martian clays (~3 Ga) (Mahaffy *et al.*, 2015).

The D/H ratio for hydrogen in the protosolar nebula estimated from the solar composition is about 5 to 7 times lower than the SMOW value (Geiss and Gloeckler, 1998). Therefore, considering only D/H ratios, the Earth's oceans were likely supplied by carbonaceous chondrites or a combination of comets and protosolar nebula.

However, the origin of the Earth's water is not so simple, if other geochemical constraints are considered. For example, using the Os isotopic compositions of the mantle and of meteorites, Meisel *et al.* (1996, 2001) argued that the material of the late veneer is more similar to that of enstatite chondrites or ordinary chondrites than to that of carbonaceous chondrites, meaning that the main source of the late veneer was not carbonaceous chondrites.

Another example is the Xe/Kr ratio. The Xe/Kr ratios on Earth and also on Mars ($^{130}\text{Xe}/^{84}\text{Kr} = 8.4 \times 10^{-3}$ for Earth) are much lower than that in any of the chondrites (2.0×10^{-1} for carbonaceous chondrites). This is often termed the missing xenon problem (e.g., Ozima and Podosek, 2002). In order to solve this problem, a source with low Xe/Kr ratio is required. Since low-temperature experiments have shown that amorphous water ice can trap significant amounts of noble gases, and that the associated Xe/Kr ratio is very low (Owen *et al.*, 1992; Barnun and Owen, 1998), comets likely played an impor-

tant role in supplying noble gases to Earth. Dauphas (2003) has pointed out that the Earth's volatiles have the dual origins, coming from both carbonaceous chondrites and comets, based on noble gas abundances. Considering both D/H ratios and the other geochemical constraints, comets alone cannot account for the entire water budget of Earth, nor can meteorites and water from the primordial nebula. The most likely means by which water was delivered to Earth, which also agrees with dynamical models for the formation of terrestrial planets, involves asteroids from the outer part of the asteroid belt (e.g., Raymond *et al.*, 2005, 2009; Izidoro *et al.*, 2013, 2014; Walsh *et al.*, 2011).

SUMMARY

The presence of oceans distinguishes Earth from the other planets in our solar system. Water is also essential for the origin and evolution of life, the stability of the surface environment and the evolution of the planetary interior. Although the mass of the Earth's oceans is very small (0.023 wt%) compared to the mass of entire Earth, our planet potentially has water in its interior equal to many times the ocean mass. The estimated amount of water in the Earth's mantle ranges from 1 to $10 M_{\text{oce}}$, and the Earth's core could contain up to the equivalent of $100 M_{\text{oce}}$ as hydrogen.

The Earth's oceans have existed throughout the planet's history. Planetary formation theory predicts that water supply on Earth occurred during its formation with much less after its formation. The origin of the Earth's water is still much in question, because of several uncertainties concerning the planet formation process, including the position of the snow line in the protoplanetary disk, the lifetime of the nebula gases, the timing of the formation of Jupiter and migration of planets. Fortunately, recent observations of the birth place of planets in extrasolar systems by large telescopes such as ALMA (Atacama Large Millimeter Array) have begun to reduce some of these uncertainties concerning the planet formation process (e.g., Wyatt, 2008; Dutrey *et al.*, 2014; Genda *et al.*, 2015b).

The number of detected extrasolar planets, which are planets around other stars, has increased as observation technologies have advanced, and now exceeds 1000 (Fabrycky *et al.*, 2014). Extrasolar planets with masses comparable to that of Earth have also been recently detected (Weiss and Marcy, 2014), and some are thought to be terrestrial or rocky planets based on the relationship between their mass and radius. In the near future, planets with oceans (and even life!) may be detected. By comparing Earth with these extrasolar planets, we will be able to understand more about the origin of Earth's water.

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