ASTEROIDS, COMETS AND TERRESTRIAL WATER*

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Abstract

There is no agreement on the origin of water on Earth and Mars. A number of sources have been proposed but the pieces of this puzzle do not currently fit into a coherent picture. We list various geochemical measurements that can serve as discriminators and we use them to examine the principal proposed mechanisms for delivery of terrestrial and Martian water. Important developments have occurred in our understanding of the presence of water during early and late stages of Earth's formation. It has long been thought that the region of the solar nebula where Earth formed was too dry for hydrous mineral phases to be stable and form a "wet" Earth, and that water was delivered by impacts of asteroids and/or comets with Earth after it formed. However, several recent measurements support the existence of water oceans on Earth shortly after its formation, as early as 4.3 to 4.4 x 10^9 years ago. The source or sources of this early water are not obvious at this time. Two recent mechanisms proposed for the formation of a wet early Earth are adsorption of nebular gas onto fractal dust grains in Earth's formation region and migration of hydrated silicates from the outer asteroid belt region of the solar nebula. On the other hand, late stage delivery of significant quantities of water from asteroidal and cometary

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sources appears less likely that previously thought. Isotopic and molecular ratio considerations do not favor asteroids or comets as the main contributors to what is commonly termed the "late veneer" in Earth's formation. There are three important caveats to this last statement. First, our measurement of the composition of comets and asteroids may not be representative of their bulk atomic, isotopic and molecular composition. Second, comets and asteroids currently sampled spectroscopically and by meteorites may be unlike those falling to Earth during its formation. Third, the processes involved in planetary accretion, degassing, and the evolution of a hydrosphere and atmosphere are complex and may have fractionated the chemical and isotopic signatures of the source(s) of water. Independent of the role comets and asteroids may have played in the delivery of water, they appear to have been the principal source of organic compounds once the Earth's crust had solidified.

1. Introduction

Are Earth-like planets with water oceans rare or common among planetary systems? Although we do not yet have an answer to this question form direct observations, the study of the origin of water on Earth and Mars can provide important insights. Current evidence points toward a variety of mechanisms for the delivery of water to Earth and Mars. Most if not all of these delivery mechanisms are expected to be common to the formation of other planetary systems. Hence, the presence of water on Earth, and its role in the origin of life, does not appear to be unique.

Water is a common chemical compound in our galaxy and in our solar system. In addition to Earth, it has been identified in asteroids, comets, meteorites, Mars, in the atmospheres, rings and moons of giant planets, and there is indirect evidence for it in the poles of our Moon and of Mercury. The high deuterium to hydrogen (D/H) ratio of Venus' atmosphere has been interpreted as evidence for Venus having had far more water in the past than is present today.

Here, we address the origin of terrestrial and Martian water. There is no agreement on the origin of water on Earth and Mars. Possible sources include capture of solar nebula gas, adsorption of water from gas onto grains in the accretion regions of these planets, accretion of hydrous minerals forming in the inner solar system, hydrous silicates migrating from the asteroid belt, and impacts with comets and hydrous asteroids. Other reviews that discuss this topic include Mottl et al. (2007), Pepin and Porcelli (2006, 2002), Righter et al. (2006), Robert (2006, 2003) Drake (2005), Campins et al. (2004), Lunine et al. (2003), Drake and Righter (2002) and Robert et al. (2000).

We have information on Martian water mainly through studies of the Martian meteorites and in situ measurements by spacecraft. However, Mars presents unique challenges because compositional information is more limited than for Earth. An important example is the global value of the D/H ratio for Martian water. It is possible that we do not know Mars' intrinsic D/H isotopic ratio. Unlike Earth, Mars lacks plate tectonics and, hence, has no means of cycling water between mantle and crust. The Martian meteorites we measure on Earth could be sampling water delivered to Mars by cometary and asteroidal impacts subsequent to planetary formation. Note, however, that the contrary has been argued (Watson [Leshin] et al., 1994), i.e., that Martian meteorites provide evidence for an intrinsic Martian mantle D/H ratio up to 50% higher than Earth's mantle (see Figure 1). Because we know most about water on Earth, the main focus of this paper will be examining the origin of such water, and whenever possible we address the case of Martian water.

2. Water on Earth

2.1 Accretion History:

The accretion of the Earth was dominated by a violent series of events. Dynamical theory of planetary accretion points to a hierarchy of accreting planetesimals, with the largest object accreting at any given time during the growth of a planet being one tenth to one third of the mass of the growing planet (Wetherill, 1985; Chambers, 2001). During the later stages of accretion, these collisions deposited enough energy to at least partly (and possibly completely) melt the Earth. Earth probably experienced serial magma ocean events. The most massive impact ejected material into Earth orbit; this disk of ejected material is thought to have subsequently accreted to form the Moon (e.g., Canup and Asphaug, 2001). Even after the formation of Earth's Moon an intense bombardment (of smaller yet substantial objects) continued, this period is commonly known as the "late heavy bombardment" and ended about 3.9 Ga ago (e.g., Tsiganis et al. 2005).

Metal delivered by accreting planetesimals sank through these serial magma oceans and ponded at their bases for some period of time before transiting diapirically through the lower mantle to the center of the planet. Metal appears to have equilibrated with silicate at the base of the magma ocean. The mean depth calculated corresponds to at least the depth of the current upper mantle/lower mantle boundary of the Earth (Drake, 2000). That depth probably represents some ensemble average memory of metal-silicate equilibrium in a series of magma oceans and should not be taken as the literal depth of the last magma ocean. Comparable conclusions about magma oceans can be drawn for the Moon, Mars, and the asteroid Vesta (Righter and Drake, 1996). As

discussed below, a primitive atmosphere and water ocean appear to have formed very early in Earth's history. Core formation, magma ocean solidification, water ocean and atmospheric outgassing were essentially complete by 4.45 Ga ago.

2.2 Evidence for an Early Water Ocean:

It had long been thought that in the solar nebula the accretion disk at one astronomical unit (AU) from the Sun was too hot for hydrous phases to be stable (e.g., Boss, 1998), and that water was delivered by impacts of asteroids and/or comets with Earth after it formed. However, recent geochemical evidence increasingly argues against asteroids and comets being the main sources of Earth's water and the evidence points to the Earth accreting "wet" throughout its growth (Drake and Righter, 2002; Drake, 2005, Mottl et al. 2007). In either case, the Earth may have had water oceans very early in its history. Several arguments support the existence of these early oceans on Earth.

The different reservoirs of $^{129}Xe/^{132}Xe$ in the atmosphere, and the mid-ocean ridge basalt (MORB) source support the presence of an early ocean. The isotope ^{129}I decays to ^{129}Xe with a half-life of about 16 Ma and is produced only by stellar nucleosynthesis in precursor astrophysical environments. Distinct $^{129}Xe/^{132}Xe$ reservoirs on Earth (and Mars) must have formed within 100 Ma of the last event of astrophysical nucleosynthesis of ^{129}I. It is difficult, although not impossible, to fractionate I from Xe by purely magmatic processes (Musselwhite and Drake, 2000); the problem is that I and Xe are both volatile and incompatible (they both have low vaporization temperatures and both prefer magmas to solid mantle), although Xe is a

little less incompatible. However, water is extremely effective at fractionating I from Xe (Musselwhite *et al.*, 1991). This is because I dissolves in liquid water (it is a halogen) while Xe bubbles through as a gas. If accretion ceased while [129]I still existed and any magma ocean solidified, liquid water could become stable at the Earth's surface. Consequently, as Musselwhite (1995) showed, outgassed [129]I could be recycled hydrothermally into the oceanic crust and subducted back into a mantle reservoir, by then partially degassed of Xe. Subsequent decay of [129]I into [129]Xe would give a MORB source an elevated [129]Xe/[132]Xe ratio relative to the earlier outgassed atmosphere (Figure 2). A related conclusion was drawn for Mars (Musselwhite et al., 1991). Therefore, based on the observed elevated [129]Xe/[132]Xe in MORB, it can be inferred that the Earth had a primitive atmosphere, large bodies of water, and a tectonic subduction zone by 4.45 Ga ago.

Further evidence for the existence of an early water ocean on Earth comes from detrital zircons. Wilde et al. (2001) and Mojzsis et al. (2001) independently reported zircons of 4.4 Ga age and 4.3 Ga age respectively. On the basis of magmatic oxygen isotope ratios and micro-inclusions of SiO_2, these authors concluded that the zircons formed from magmas that interacted with liquid water. Wilde et al. (2001) specifically suggest that the 4.4 Ga zircons represent the earliest evidence of both continental crust and water oceans on Earth. Support for this argument was provided by Watson and Harrison (2005), who used a geothermometer based on the Ti-content of zircons to conclude that they crystallized at ~700 °C, a temperature indistinguishable from granitoid zircon growth today. In other words, water-bearing evolved magmas appear to have been present on Earth within 200 Ma of solar system formation. The implication is that modern

patterns of crust formation, erosion, and sediment formation had been established prior to 4.4 Ga, implying liquid water oceans already existed.

3. Proposed Sources of Water and Methods of Discrimination

In principle, it should be possible to determine the main sources of and relative contributions to Earth's water, if they have distinct chemical and isotopic signatures. In practice this task can be made more difficult by the complex formation and evolution histories of Earth and its likely water sources.

3.1 Discriminators

Chemical and isotopic signatures that are used as discriminators include the following.

- The D/H ratio of water in Earth, Mars, comets, meteorites, and the solar nebula.

- The relative abundances and isotopic ratios for noble gases on Earth, Mars meteorites, comets and the Sun.

- The ratio of noble gases to water on Earth, meteorites and comets.

- The isotopic composition of the highly siderophile (very strongly metal-seeking) element Os in Earth's primitive upper mantle (PUM), in the Martian mantle, and in meteorites.

3.1.1 D/H Ratios

Deuterium is a primordial product of Big Bang nucleosynthesis, formed in the early universe. Nuclear reactions in stars convert D into He. Cycling of primordial matter through stars tends to lower the D/H ratio of the interstellar medium over cosmological time. However, chemical and physical mass fractionation processes can produce local enhancements in the D/H ratio. For example, low-temperature ion-molecule reactions in the cores of molecular clouds can enhance the D/H ratio in icy grains by as much as two orders of magnitude above that observed in the interstellar medium (*e.g.*, Gensheimer *et al.* 1996). In our solar system, there is evidence for more than one primitive reservoir of hydrogen (Drouart et al. 1999, Mousis et al. 2000, Robert 2001, Hersant *et al.* 2001 and references therein). The solar nebula gas D/H ratio is estimated from observations of CH_4 in Jupiter and Saturn to be $2.1 \pm 0.4 \times 10^{-5}$ (Lellouch *et al.* 2001). Jupiter and Saturn likely obtained most of their hydrogen directly from solar nebula gas. This estimate is also consistent with protosolar D/H value inferred from the solar wind implanted into lunar soils; Geiss and Gloecker (1998). A second reservoir, enriched in D compared with the solar nebula gas, contributed to bodies that accreted from solid grains, including comets and meteorites.

We have high D/H ratios (relative to Earth's water) measured spectroscopically from water in three comets (all from the Oort cloud), Halley ($3.2 \pm 0.1 \times 10^{-4}$, Eberhardt *et al.* 1995); Hyakutake ($2.9 \pm 1.0 \times 10^{-4}$, Bockelée-Morvan *et al.*, 1998); and Hale-Bopp ($3.3 \pm 0.8 \times 10^{-4}$, Meier *et al.*1998). These are all about twice the D/H ratio for terrestrial water (1.49×10^{-4}; Lecuyer *et al.,* 1998), and about fifteen times the value for the solar nebula gas ($2.1 \pm 0.4 \times 10^{-5}$,

Lellouch *et al.*, 2001). These comet D/H ratios are consistent with the range of values for "hot cores" of dense molecular clouds (2 to 6 x 10^{-4}, Gensheimer *et al.,* 1996). Carbonaceous chondrites have the highest water abundance of all meteorites (up to 17 wt% H_2O; Jarosewich, 1990). Their D/H ratios range from 1.20 x 10^{-4} to 3.2 x10^{-4} (Lecuyer et al., 1998). The largest D-enrichment in a water-bearing mineral in a meteorite was measured at 7.3 ± 1.2 x10^{-4} in the LL3 chondrite Semarkona (Deloule and Robert 1995). These results are illustrated in Figure 1.

The measurement of the D/H ratio of water in three comets is a significant development. Different authors, however, interpret these ratios in very different ways. Some (*e.g.*, Dauphas *et al.*, 2000; Morbidelli *et al.*, 2000; Drake and Righter, 2002; Robert, 2001) consider the high D/H ratio in these comets as evidence against a cometary origin of most of the terrestrial water. Others (*e.g.*, Delsemme, 2000, Owen and Bar-Nun, 2001) argue that comets are the main reservoir of deuterium-rich water that raised the terrestrial D/H a factor of six above the protosolar value. Complicating the matter further, laboratory measurements of the D/H ratio in sublimating ices have shown that D/H isotope fractionation can occur during sublimation (Weirich et al., 2004, Moores et al., 2005). During sublimation of water ice samples in a vacuum the D/H ratio of the evolved gas varies with time; this ratio can increase or decrease relative to the initial D/H ratio, depending on the nature of the sample. The root cause is interpreted to be differential diffusion and sublimation of HDO and H_2O (HDO is a water molecule with one deuterium and one hydrogen atom instead of two hydrogen atoms). This result implies that spectroscopically measured D/H ratios from cometary comae may not be representative of the bulk cometary values.

3.1.2 Noble Gases

Noble gases are chemically inert and highly volatile. Hence they probably arrive at a planet along with other volatiles, quickly move to the planet's atmosphere, and in bulk tend to avoid the chemical complications of planetary evolution. Thus, the noble gas characteristics of a planetary atmosphere can provide tracing information to the source of the planet's volatiles. Figure 3 shows the abundances of noble gases in Venus, Earth and Mars compared with solar abundances as well as those from two kinds of meteorites. Note that the proportions of Ar, Kr, and Xe in the atmospheres of Earth and Mars are remarkably similar, and also significantly different from the relative abundance patterns found in meteorites or in the Sun (determined from solar wind).

We do not know much about noble gases in comets. Some of the measurements we do have appear contradictory. Krasnopolsky *et al*. (1997) reported an upper limit in comet Hale-Bopp of 0.5% of the solar Ne/O ratio. Stern *et al*. (2000) reported a tentative Ar detection in comet Hale-Bopp at a roughly solar Ar/O ratio. Weaver *et al*. (2002) reported upper limits for Ar/O of <10% and <8% respectively of the solar value in comets LINEAR 2001 A2 and LINEAR 2000 WM1. All these observations have been made of comets from the Oort cloud. The more sensitive upper limits for Ar in the LINEAR comets are not consistent with the detection reported by Stern *et al*. (2000) in comet Hale-Bopp. At this point it is not clear if comet Hale-Bopp was unusually rich in Ar, or if the tentative detection is somehow flawed. We return to this issue in sections 3.2.3 and 3.2.4.

3.1.3 Siderophile Elements in Earth's Mantle

The relatively high abundances of highly siderophile elements (HSEs), at 0.003 x CI, in Earth's primitive upper mantle and their roughly chondritic element ratios suggest that these elements arrived after Earth's core formation had ceased (e.g., Drake and Righter, 2002). Had these elements arrived sooner, they would have been quantitatively extracted into Earth's core. This material is commonly termed the "late veneer". Drake and Righter (2002) and Righter et al. (2006) argue that Earth-building materials shared some but not all properties with extant meteorites, in other words, no primitive material similar to Earth's mantle is currently in our meteorite collections[1]. More specifically, Os isotopes can be used to constrain the origin of the late veneer. Carbonaceous chondrites, the only abundant water-bearing meteorites, have a significantly lower $^{187}Os/^{188}Os$ ratio of 0.1265 than Earth's primitive upper mantle value of 0.1295, essentially ruling out their parent bodies as the main source of the late veneer (Figure 4). The Earth's mantle $^{187}Os/^{188}Os$ ratio overlaps anhydrous ordinary chondrites and is distinctly higher than anhydrous enstatite chondrites. If the objects that brought Earth its late veneer also contributed a significant amount of water, their composition had to have been different from water-bearing meteorites in our collections. It has been suggested that mixtures of anhydrous ordinary chondrites and hydrous carbonaceous chondrites could yield an appropriate Os isotopic signature for Earth. This hypothesis is certainly possible, but the same mixture would have to satisfy both $^{187}Os/^{188}Os$ ratios and D/H ratios in Earth (Figs. 1 and 4). Until recently, it appeared that Mars' primitive upper mantle could have an even higher $^{187}Os/^{188}Os$ ratio of 0.132 (Brandon

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[1] This result is consistent with dynamical models that suggest Earth accreted about half of its current mass from material that formed near Earth's location, and the other half from embryos scattered from both smaller and larger heliocentric distances (e.g., Morbidelli et al. 2000). Since most meteorites come from the asteroid belt (between 2 and 3.2 AU), it is not surprising that the building blocks of Earth are not properly sampled by meteorites.

et al., 2005). However, new estimates (Muralidharan et al. 2008) suggest the value is more terrestrial (orange and grey areas of the Figure 4), and therefore, more compatible with a contribution to Mars by the same source of Earth's late veneer.

3.2 Sources

In this section we examine the principal proposed sources of terrestrial and Martian water in the light of these discriminators. We evaluate the possible contribution from each source using the discriminators discussed in section 3.1.

3.2.1 Primordial Gas Captured from the Solar Nebula

It has been argued that a primordial atmosphere could not have been captured directly from the solar nebula, principally because of Earth's D/H ratio in water and the noble gas abundances. However, Campins et al. (2004) and Mottl et al. (2007) point out that the processes involved in planetary accretion, degassing, and the evolution of a hydrosphere and atmosphere are complex and may have fractionated the chemical and isotopic signatures of the source(s) of water. Hydrogen, for example, may be an important constituent in the outer, and possibly inner, core of Earth (e.g., Okuchi 1997, 1998). If H and D were fractionated in that process, the residual D/H ratio in the hydrosphere may not reflect that of the original source. Following accretion, the surface of the Earth continued to be modified by large impacting asteroids and comets (Sections 3.2.3 and 3.2.4). Large impact events have the capacity to completely volatilize any oceans (Zahnle and Sleep, 1997) and blow off portions of Earth's atmosphere (Melosh and Vickery, 1989, Zahnle 2006). Fractionation of D/H and noble gas/water ratios may occur as a consequence of impact processes, which may also mask the signatures of the original source material.

The terrestrial planets grew in an accretion disk of gas and dust grains. Hydrogen, He, and O_2 dominated the gas in which the dust was bathed. Some of that H_2 and O_2 combined to make water vapor. If thermodynamic equilibrium was attained, there were about two Earth masses of water vapor in the accretion disk inside of 3 AU (Drake, 2005). The mass of the Earth is 5×10^{27} g. The mass of one Earth ocean is 1.4×10^{24} g. The extreme maximum estimate for the amount of water in the Earth is about 50 Earth oceans (Abe *et al.*, 2000), with most estimates being 10 Earth oceans or less. For example, an estimate based on the water storage potential of minerals in the silicate Earth is about 5 – 6 Earth oceans (Ohtani, 2005). Thus the mass of water vapor available in the region of the terrestrial planets far exceeded the mass of water accreted. Could water vapor be adsorbed onto grains before the gas in the inner solar system was dissipated? Stimpfl *et al.* (2004) have examined the role of physisorption by modeling the adsorption of water on to grains at 1000 °K, 700 °K, and 500 °K using a Monte Carlo simulation. Stimpfl *et al.* (2004) "exploded" the Earth into 0.1 μm spheres of volume equal to Earth, recognizing that grains in the accretion disk are not spherical and would be fractal in nature. If the surface area of the fractal grain was 100 times that of a sphere of corresponding volume, then one quarter of an ocean of water could be adsorbed at 1000 °K, one Earth ocean could be adsorbed at 700 °K, and three Earth oceans could be adsorbed at 500 °K. This work is discussed in more detail in Drake (2005). There are also issues of retention of water as the grains collide and grow to make planets. However, it is clear that volatiles are not completely outgassed even in planetary scale collisions. For example, primordial ³He, far more volatile than water, is still outgassing from Earth's mantle 4.5 Ga after an almost grown Earth collided with a Mars-sized body to make the Moon. Stimpfl *et al.* (2004) showed that the efficiency of adsorption of water increases as

temperature decreases, that is, the process should have been more efficient further from the Sun than closer to the Sun. Thus, it is likely that Mars, Earth, and Venus all accreted some water by adsorption, with Mars accreting the most both because of its greater distance from the Sun and the lower energy of collisions during accretion because of its smaller final mass. The current differences in the apparent water abundances among the terrestrial planets are probably the result of both different initial inventories and subsequent geologic and atmospheric processing.

There is an interesting consequence for the evolution of planetary redox states if the terrestrial planets accreted "wet". Okuchi (1997) showed that when Fe-metal and water were compressed to 30-100 kbars and heated to 1200 °C – 1500 °C, iron hydride formed. In a magma ocean environment, metal sinking to form planetary cores should contain H, and OH should be left behind in the molten silicate. As more metal was delivered to the planet as it accreted, more H would be extracted into the core and more OH liberated in the silicate mantle. Thus planetary mantles should become progressively more oxidized with time, perhaps explaining the high redox states relative to the iron – wüstite buffer (the iron – wüstite buffer is a measure of the oxygen fugacity as a function of temperatue). This process might explain the correlation of the degree of oxidation of silicate mantles with planet mass (Righter et al., 2006).

3.2.3 Comets

Comets were long considered the most likely source of water in the terrestrial planets. A cometary source was attractive because it is widely believed that the inner solar system was too hot for hydrous phases to be thermodynamically stable (Boss, 1998). Thus an exogenous source of water was needed. There are elemental and isotopic reasons why at best 50% and, most probably, a small percentage of water accreted to Earth from cometary impacts (Drake and Righter, 2002). Figure 1 compares the isotopic composition of hydrogen in Earth, Mars, three Oort Cloud comets, and various early solar system estimates. It is clear that 100% of Earth's water did not come from Oort Cloud comets with D/H ratios like the three comets measured so far. D/H ratios in Martian meteorites do agree with the three cometary values (Figure 1). That may reflect the impact of comets onto the Martian surface in a non-plate tectonics environment that precludes recycling of surface material into the Martian mantle (Drake 2005). Conversely, there are models (Lunine et al. 2003) that have asteroids and comets from beyond 2.5 AU as the main source of Mars' water.

So what limits the cometary contribution to Earth's water? Consider, for example, that perhaps Earth accreted some hydrous phases or adsorbed water, and some amount of additional water came from comets. Indigenous Earth water could have had D/H ratios representative of the inner solar system, i.e., low values because of relatively high nebular temperatures, perhaps like protosolar hydrogen ($2\text{-}3 \times 10^{-5}$, Lecluse and Robert, 1994) in which case a cometary contribution of up to 50% is possible. Alternatively, indigenous Earth water could have had D/H ratios representative of a protosolar water component identified in meteorites ($\sim 9 \times 10^{-5}$, Deloule

and Robert 1995), in which case there could be as little as a 10-15% cometary contribution (Owen and Bar-Nun, 2000). There are caveats to using cometary D/H ratios to limit the delivery of cometary water to Earth. First, we do not know that Oort Cloud comets Halley, Hale-Bopp, and Hyakutake are representative of all comets. Certainly they are unlikely to be representative of Kuiper Belt objects, the source of Jupiter family comets, as Oort Cloud comets formed in the region of the giant planets and were ejected, while Kuiper Belt objects have always resided beyond the orbits of the giant planets. Second, the D/H measurements available are not of the solid nucleus, but of gases emitted during sublimation. As mentioned in Section 3.1, differential diffusion and sublimation of HDO and H_2O may make such measurements unrepresentative of the bulk comet. The D/H ratio would be expected to rise in diffusion and sublimation, as has been confirmed in preliminary laboratory experiments on pure water ice (Weirich et al., 2004). Lower bulk D/H ratios would increase the allowable amount of cometary water. Intriguing experiments on mixtures of water ice and TiO_2 grains by Moores et al. (2005) suggest that D/H ratios could be lowered in sublimates. Third, the D/H ratios of organics and hydrated silicates in comets are currently unknown. Note, however, that D/H ratios up to 50 times higher than Vienna Standard Mean Ocean Water (VSMOW) have been measured in some chondritic porous interplanetary dust particles (CP-IDPs) which may have had cometary origins (Messenger, 2000). Higher aggregate D/H ratios of comets would decrease the allowable cometary contribution to Earth's water.

Delivery of water from comets can also be evaluated in light of other cometary chemical data. If one assumes 50% of Earth's water was derived from comets (the maximum amount permitted by D/H ratios), and an Ar/H_2O ratio of 1.2 x 10^{-7} in the bulk Earth, then comets like Hale-Bopp

(with a solar ratio of Ar/H_2O, Stern et al., 2000) would bring 2×10^4 more Ar than is presently in the Earth's atmosphere (Swindle and Kring, 2001). It is unclear if this measurement of comet Hale-Bopp is applicable to all comets. However, the true Ar/O ratios in comets would have to be at least three orders of magnitude below solar in order to be consistent with the Ar abundance of the Earth's atmosphere. Another approach to estimating the contribution of cometary materials to Earth's water budget can be made by considering the implications for the abundances of noble metals and noble gases. Dauphas and Marty (2002) show that the total mass of cometary and asteroidal material accreting to Earth after core formation is $0.7 - 2.7 \times 10^{25}$g and that comets contribute <0.001 by mass or $<0.7 - 2.7 \times 10^{22}$g. Given that the minimum mass of water in the Earth, one Earth ocean, is 1.4×10^{24}g, this argument suggests that comets can contribute less than 1% of Earth's water.

3.2.4. Asteroids

Asteroids are a plausible source of water based on dynamical arguments. Morbidelli et al. (2000) have shown that up to 15% of the mass of the Earth could be accreted late in Earth's growth by collision of one or a few asteroids originating in the Main Belt. This hypothesis is difficult to test, as it could involve a single, unique event. However, there are strong geochemical arguments against a significant contribution of water from asteroids, unless one postulates that Earth was hit by a hydrous asteroid unlike any falling to Earth today as sampled by meteorites. As mentioned in section 3.1.3, a late addition of water to Earth must be accompanied by other chemical elements such as Os. Since Earth's primitive upper mantle has a significantly higher $^{187}Os/^{188}Os$ ratio than the water-bearing meteorites (carbonaceous

chondrites), this effectively rules them out as the main source of the late veneer (Figure 4). However, mixtures of anhydrous ordinary chondrites and hydrous carbonaceous chondrites could yield an appropriate Os isotopic signature for Earth, but the same mixture would have to satisfy both $^{187}Os/^{188}Os$ ratios and D/H ratios in Earth (Figs. 1 and 4). Another caveat to consider is that thermal processing of asteroids was occurring 4.5 Ga ago. One cannot exclude the possibility that ordinary chondrites once contained water and those falling to Earth today have lost their water by metamorphism, even though it was still present 4.5 Ga ago. However, the preservation of aqueous alteration products in some carbonaceous chondrites (McSween, 1979) suggests that loss of water from initially hydrous asteroids is unlikely to proceed to the anhydrous limit.

3.2.5 Early Accretion of Water from Inward Migration of Hydrous Silicates

Most solar nebula models suggested that the growth zones of the terrestrial planets were too hot for hydrous minerals to form (e.g., Cyr et al., 1998; Delsemme, 2000; Cuzzi and Zahnle, 2004). Ciesla and Lauretta (2005) suggest that hydrous minerals were formed in the outer asteroid belt region of the solar nebula and were then transported to the hotter regions of the nebula (i.e., Earth and Mars) by gas drag, where they were incorporated into the planetesimals that formed there. These hydrated minerals were able to survive for long periods in hotter regions due to sluggish dehydration kinetics. Note that this mechanism differs from the delivery of water by stochastic impacts with large planetary embryos originating in the outer asteroid belt region (Section 3.2.4). Drake (2005) points out that it seems unlikely that hydrous silicates could be decoupled from other minerals and transported into the inner solar system. Thus the proposed radial migration of hydrous minerals would be subject to the same objection involving Os

isotopes (Section 3.2.4), unless the hydrous silicates arrived prior to the differentiation of Earth, as suggested by Ciesla and Lauretta (2005).

3.3. Water and Organics:

It has been postulated that water and organics were delivered from the same cometary and/or asteroidal source (e.g., Chyba, 1993; Delsemme, 2000). In light of the new evidence, such combined delivery seems less likely. In addition to comets and asteroids being inconsistent with some geochemical properties of Earth, it is unlikely that a complex organic material would have survived the magma ocean accompanying the formation of the Moon at the end of accretion of the Earth (Drake, 2000). However, it seems possible that complex organic material may have been delivered to Earth after it formed and liquid water oceans became stable. Comets, which are known to be rich in organic molecules, have been postulated to be the principal source of terrestrial amino acids (Pierazzo and Chyba, 1999; Chyba, 1993). Some meteorites are also rich in carbon and organic compounds, hence, asteroids may have also contributed significantly to Earth's organic inventory. In fact, Kring and Cohen (2002) point out that during the late heavy bombardment, asteroidal material probably delivered a large mass of organic material to Earth's surface, as much as 160 times larger than that in the total land biomass today. Even if some of the organic molecules were dissociated during the impacts, Kring and Cohen (2002) propose the formation of impact-generated hydrothermal regions with lifetimes up to 10^6 years, where complex organic molecules might reassemble.

4. Outstanding Challenges

Although a number of sources for terrestrial and Martian water have been proposed, the pieces of this puzzle do not currently fit into a coherent picture. Many issues remain to be resolved; below we list some of the most important.

1. The D/H ratio of the nebular gas is inferred from spectroscopic measurements of CH_4 in the atmospheres of Jupiter and Saturn to be $2.1 \pm 0.4 \times 10^{-5}$ (Lellouch et al., 2001), much lower than VSMOW (the D/H ratio for Vienna Standard Mean Ocean Water). If the nebular D/H ratio really is as low as implied by the Jovian and Saturnian atmospheres[2], then mechanisms to raise the D/H ratio of nebular gas from solar to terrestrial (as VSMOW) are needed.

2. It is possible that the D/H and Ar/O ratios measured in cometary comae are not truly representative of cometary interiors. Reconnaissance experiments have shown that D/H ratios in laboratory experiments can increase or decrease with time due to differential diffusion and sublimation, depending on the physical nature of the starting material (Weirich et al., 2004; Moores et al., 2005). Further, published measurements of Ar/O ratios in comets are either upper limits or 3-sigma detection limits and seem inconsistent with each other. Depending on the location of Ar inside comets, Ar/O ratios may also be unrepresentative of the bulk cometary composition. The successful Deep Impact mission is the first attempt to expose fresh cometary interior material for spectral analysis with ground-based and space-based high spectral resolution

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[2] Spectroscopic or direct measurements of solar D/H are not representative of the original bulk composition of the nebular source because practically all of the Sun's deuterium has been fused to make He.

spectrometers. Unfortunately, improvements in our understanding of cometary D/H ratios and Ar/O ratios not expected from the Deep Impact results.

3. The key argument against an asteroidal source of Earth's water is that the Os isotopic composition of Earth's primitive upper mantle matches that of anhydrous ordinary chondrites, not hydrous carbonaceous chondrites. But are the parent bodies of the ordinary chondrites anhydrous? Could ordinary chondritic meteorites be derived from the metamorphosed outer parts of hydrous asteroids, in which case impact of a bulk asteroid could deliver water? It is probable that spacecraft spectral examination of very deep impact basins in S-type asteroids will be needed to address this question.

4. A related question is why there are any anhydrous primordial bodies, such as the parent bodies of anhydrous primitive meteorites, in the solar system if adsorption of water from gas in the accretion disk was an efficient process, as preliminary calculations suggest it might have been.

5. The timing of loss of gas from the accretion disk in the region of the terrestrial planets is unknown. For adsorption to be efficient, nebular gas must persist long enough for grains to adsorb water. Radial migration of hydrous silicates also depends on the presence of gas. The timing of loss of gas from the accretion disk will be intimately connected to the currently unknown mechanism of loss.

Acknowledgments

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FIGURE CAPTIONS

Figure 1. The D/H ratios in H_2O in three comets, meteorites, Earth (Vienna standard mean ocean water - VSMOW), protosolar H_2, and Mars. "CC" = carbonaceous chondrite meteorites, "LL3-IW" = interstellar water in Semarkona meteorite, "LL3-PS" = protostellar water in Semarkona meteorite. After Drake and Righter (2002).

Figure 2. Cartoon illustrating outgassing of I and Xe while [129]I was still available. Xenon bubbles through the water ocean into the atmosphere. [129]I dissolves in water and is recycled hydrothermally into the crust and subducted back into the mantle. Subsequent decay of [129]I leads to mid-ocean ridge basalts (MORB) being erupted with elevated [129]Xe/[132]Xe compared to the atmosphere. Separate Xe reservoirs imply fractionation of I from Xe within 100 Ma after nucleosynthesis of [129]I, possibly by water oceans. After Musselwhite (1995).

Figure 3. Noble gases in Venus, Earth, Mars, and meteorites. After Owen and Bar-Nun (1995).

Figure 4. [187]Os/[188]Os ratios in carbonaceous, ordinary, and enstatite chondrites, and in the Earth's primitive upper mantle (PUM), are distinct and are diagnostic of the nature of the Earth's "late veneer". In particular, Earth's PUM is different from water-bearing carbonaceous chondrites. The [187]Os/[188]Os ratios in Mars' PUM have been recently revised down (Muralidharan et al. 2008) and, although still uncertain, now overlap with those for Earth's PUM (grey area of the figure). Earlier estimates of the Martian mantle were probably compromised by incomplete dissolution of sample (A. Brandon, R. Walker, personal communications, March, 2008). This figure is modified from the original one in Drake and Righter (2002).
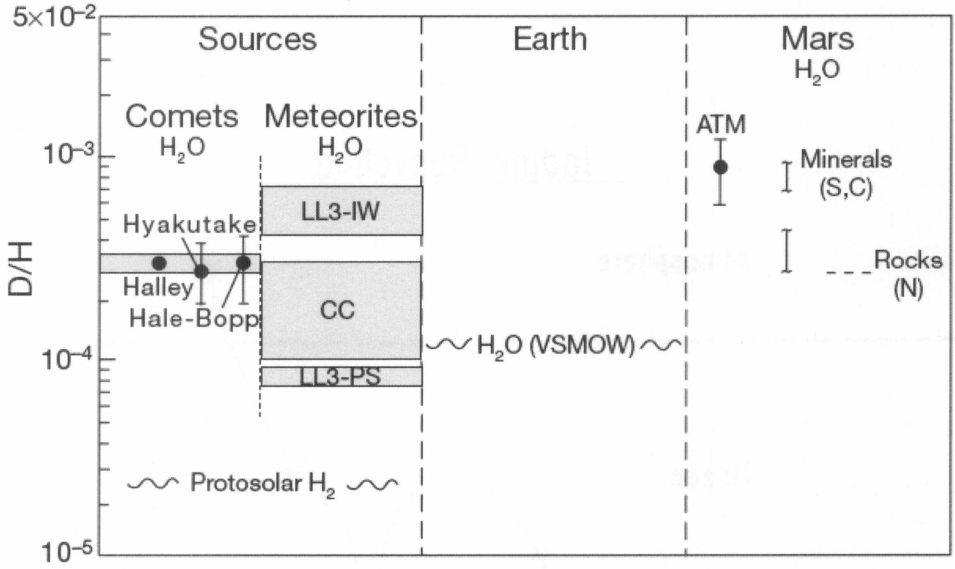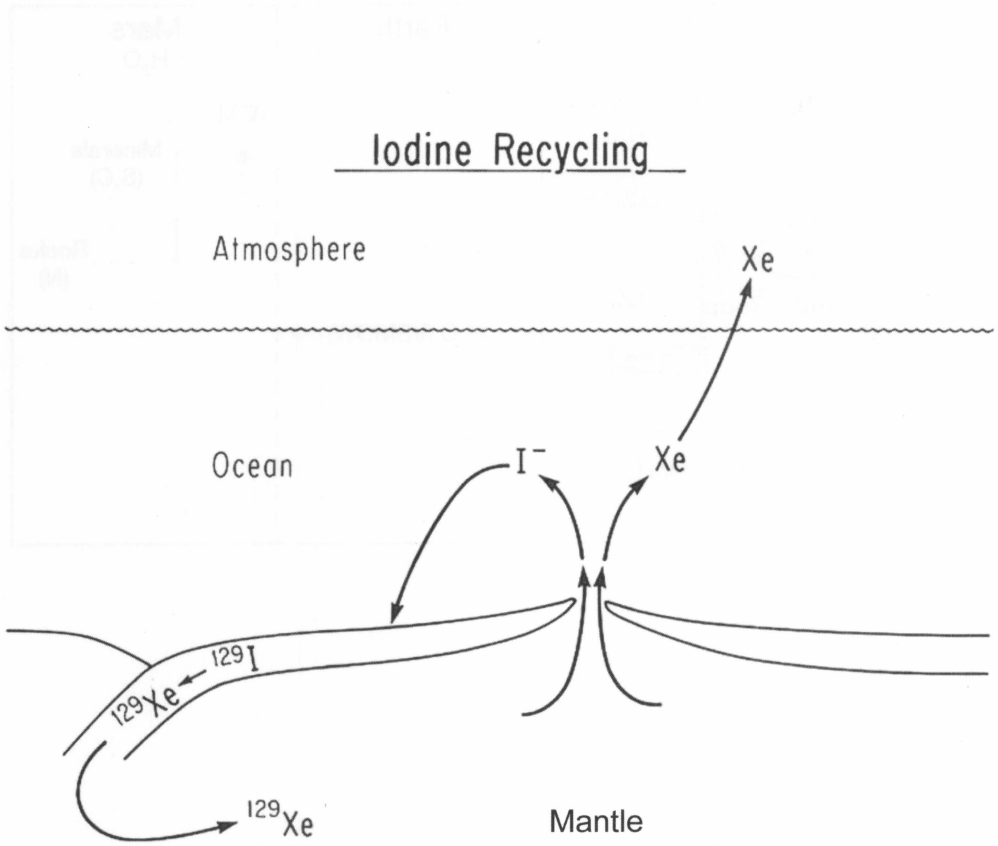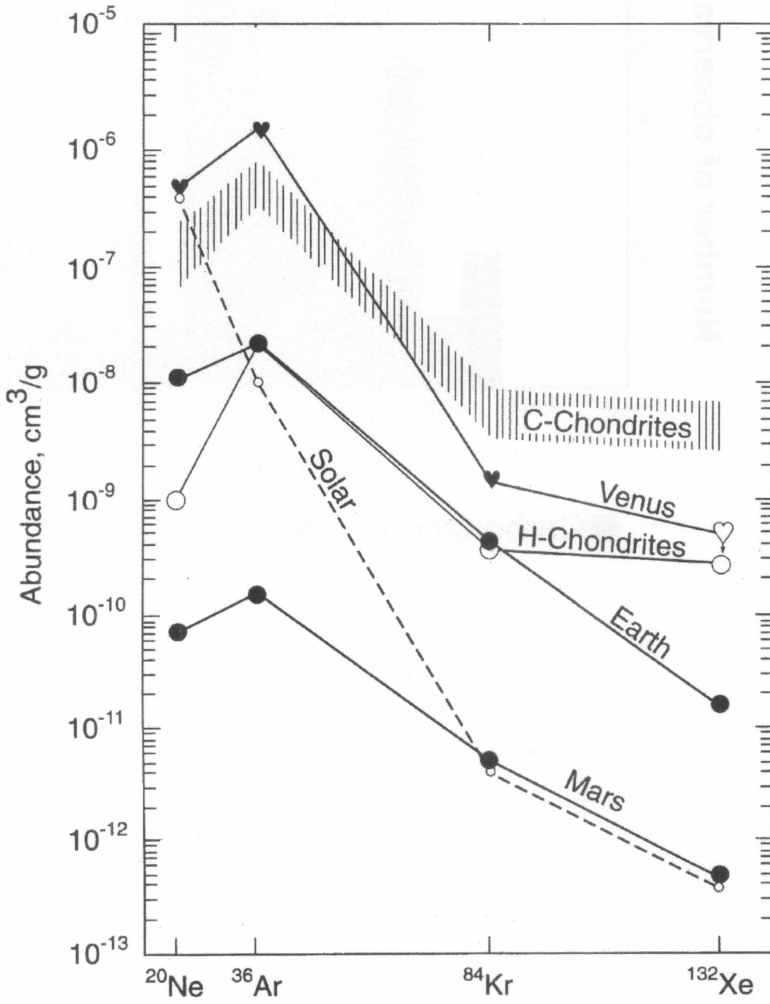
Figure 1

Figure 2

Iodine Recycling

Atmosphere

Xe

Ocean

I⁻   Xe

¹²⁹Xe ← ¹²⁹I

¹²⁹Xe

Mantle

Figure 3

Figure 3

Figure 4