

INVITED REVIEW

Water and astrobiology

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Abstract

Water is formed from two of the three most abundant elements in the universe and so is abundant in interstellar space, in our Solar System, and on Earth, where it is an essential compound for the existence of life as we know it. Water ice acts as a substrate and reactant in interstellar clouds of gas and dust, enabling the formation of organic compounds that are important precursors to life and that eventually became incorporated into comets and asteroids in the early Solar System. Laboratory experiments have allowed us to infer the reaction pathways and mechanisms by which some of these compounds are formed. In these reactions, water can act as an energy transfer medium, increasing product yields, or it can lower yields by diluting reaction centers. Water can also destroy organic compounds when water ice decomposes under ionizing radiation and the decomposition products attack the compounds; whether this happens depends critically on temperature and structure of the ice, whether crystalline or amorphous. Ice structure and temperature also largely determine its gas content. As the solar nebula collapsed, icy mantles on interstellar grains probably sublimated and then recondensed onto other grains, thus influencing the transport of energy, mass, and angular momentum in the disk. Icy grains also influenced the temperature structure of the disk because they influence mean disk opacity. Outside the “snow line” at 3–5 AU icy grains accreted to become part of comets and planetesimals that occupy the region of the outer planets, the Kuiper belt, and the Oort cloud. Water was acquired by the growing Earth by several mechanisms. Evidence from noble gas isotopes indicates that Earth achieved sufficient mass fast enough to capture an early H-rich atmosphere from the Solar nebula itself. Although the remnant of this primary atmosphere is now found only in the mantle, it may also reside in the core, which could contain most of the H on Earth (or none at all). The bulk silicate Earth contains only 500–1100 ppm H₂O, an amount small enough to explain by “wet” accretion, although most of it probably accumulated with the latter half of Earth’s mass from wetter planetary embryos originating beyond 1.5 AU. Degassing on impact delivered water to Earth’s surface, where it dissolved into a magma ocean, a process that likely saved it from loss during subsequent catastrophic impacts such as the Moon-forming giant impact, which resulted in >99% loss of the noble gas inventory. Although most of Earth’s water probably came from meteoritic material, the depletion on Earth of Xe relative to Kr strongly suggests a role for comets. The role of water in supporting life is an essential one on Earth and probably elsewhere, given the unusual properties of water compared with other potentially abundant compounds. Its dipolarity, high boiling point and heat of vaporization and, for ice, melting temperature; its expansion on freezing; and its solvent properties make it an ideal medium for life. Life originated early on Earth, indicating an abundance of water, nutrients, precursor molecules,

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substrates, and appropriate physical and chemical conditions. Life adapted quickly to (and may have originated in) extreme environments, of heat, cold, dryness, saltiness, and acidity. This adaptation to extreme conditions bodes well for the prospect of finding life elsewhere in our Solar System and in planetary systems around other stars.

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1. Introduction

The most abundant element in the Universe is H, produced in the Big Bang and burned in stars ever since. The third most abundant element (He is second) is O. These two elements combine to make H₂O, one of the most abundant constituents of the Universe and of our Solar System. Water is also one of the most important compounds for living things, for while we can imagine life in environments free of water, liquid water is an essential compound for life, as we know it, so much so that “follow the water” has become a mantra of the young science of astrobiology. Here we review the origin, occurrence, and behavior of water in the interstellar medium (ISM), in our Solar System, and on Earth, and its intimate relationship with life.

2. Water in space

2.1. Its physics and how we study it

The Big Bang that created our Universe synthesized only the three lightest elements, up to ⁷Li, and the lightest of all, hydrogen, was most abundant. Its isotopic ratio, D/H, was also set initially in the Big Bang (Table 1). Oxygen necessary to make water did not come until it was synthesized along with other heavy elements in the nuclear furnaces of the first generation of stars. Subsequently, in the cold environment of interstellar clouds of dust and gas, volatile molecules froze

out onto sub-micron-sized dust grains and formed icy mantles surrounding silicate and carbonaceous cores. Grain surface chemistry allowed formation of more complex molecules. Water ice is abundant in the interior of molecular clouds, where ~10% of oxygen atoms are bound up as water ice (Allamandola and Sandford, 1988).

Direct observation of the abundance and distribution of water in space is challenging from our terrestrial observatory because of the water vapor in Earth’s atmosphere. Additionally, UV radiation from the interstellar radiation field destroys molecules unless there is sufficient extinction of light by dust that the ice can survive. This shielding occurs in dense molecular clouds, cold aggregates of gas and dust that are the precursors of star and planet formation. Because water ice absorbs radiation strongly in the near-infrared, near 3 μm, its presence can be mapped in regions where background starlight passes through dust clouds. Water chemistry can also be inferred through observations of related species at sub-millimeter wavelengths, where there are observable spectral line emissions outside the terrestrial water absorption bands.

The gas and dust in the ISM undergoes considerable processing as it passes from a diffuse cloud into star formation, a protoplanetary disk, and ultimately to the planet-formation stage. The chemistry of deuterated molecules is highly sensitive to temperature. Deuterium (Table 1) is enriched in interstellar ices in cold dense concentrations of the ISM via complex gas-phase and gas–grain chemical reaction networks involving thousands of reactions (Brown and Millar, 1989a, b; Millar, 2003). The first phases of star formation are characterized by dramatic changes in chemical composition, including extremely enhanced molecular deuteration as heavy molecules freeze out onto grain surfaces (Ceccarelli et al., 2007).

2.2. Water in space: its role in chemical reactions

The molecular composition of interstellar space shows a great diversity, ranging from small molecules like hydrogen (H₂) to astrobiologically important species like the carbon hydrate glycolaldehyde (HOCH₂CHO) (Hollis et al., 2000). Over 130 molecular species have been observed so far (<http://www.cv.nrao.edu/Eawootten/allmols.html>). About one-third were detected as well in

Table 1. Astronomical D/H values

Source	D/H value × 10 ⁻⁶	Per mil
Big bang	16	−897
Interstellar medium	14–22	−910 to −858
Star forming regions	400–1500	+1568 to +8630
Solar Nebula/System	25	−871
Comets	310	+926
Meteorites	70–450	−550 to +1889
C-Chondrites	120–300	−229 to +926
Earth oceans (SMOW)	160	0

cometary comae, implying that some cometary material has an interstellar origin, or at least that similar chemistry takes place in the ISM and in comets. For this reason, the study of how organic material is formed in the ISM has wide repercussions in astrobiology. Comets might have delivered precursor molecules to the prebiotic Earth (Chyba et al., 1990) that would act as building blocks of biologically important molecules such as amino acids and carbon hydrates (Ehrenfreund et al., 2005).

As astronomical detection techniques have improved – from millimeter arrays to space-born infrared telescopes – increasingly complex species up to carbon hydrates (“sugars”) have been observed both in both the gas phase and ices (Snyder, 2006). Yet the degree of complexity reached by organic chemicals in space prior to their incorporation into comets and asteroids is still largely unknown. Laboratory work has been important for understanding reaction pathways and modeling reaction networks in the ISM and comets. This was underscored by recent laboratory synthesis of methanol in the gas phase (Geppert et al., 2006), which demonstrated that pathways involving gas-phase reactions are inadequate to explain its presence in many ISM environments. Methanol is, after all, a key player in the formation of complex organic molecules of astrobiological interest. These are found in the ISM, from hot cores in massive star formation regions to hot corinos, circumstellar envelopes, protoplanetary nebulae, and in comets (Ziurys, 2006). For a large number of species, the formation pathways involve gas–grain chemistry (reaction occurring on surfaces of ices coating dust grains) or chemistry in ices following deposition of ionizing radiation (cosmic rays) and/or UV photons, but little is known about these processes, even for the simplest precursors of biogenic molecules, such as methanol and formaldehyde (H_2CO). Formation of methanol in ices, e.g., is still controversial (Wada et al., 2006; Gerakines et al., 2000).

Among the molecules detected in the interstellar gas phase, structural isomers – molecules with the same chemical formula but with different arrangement among the atoms – play a crucial role in untangling their formation processes. Since the relative abundances of structural isomers depend strongly on physical and chemical conditions, isomers can act as tracers to expose temperature- and density-dependent routes for forming complex molecules. The structural isomers cyanoacetylene, isocyanoacetylene, and the carbene structure (HNCCC) played a crucial role in determining the relative importance of neutral – neutral vs. ion – molecule reactions in the gas phase of cold molecular clouds such as TMC-1 (Huang et al., 1999).

Among the organic molecules identified in the ISM, the three structural isomers of the $\text{C}_2\text{H}_4\text{O}_2$ series – acetic acid (CH_3COOH), methyl formate (HCOOCH_3), and

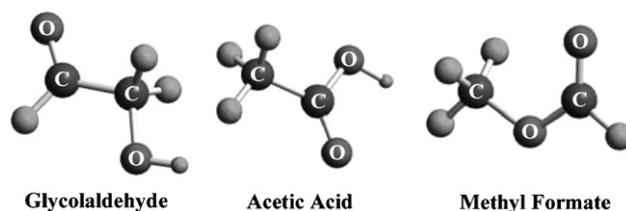


Fig. 1. Three different $\text{C}_2\text{H}_4\text{O}_2$ isomers that have been observed in the interstellar medium.

glycolaldehyde HCOCH_2OH (Fig. 1) – are considered as the key molecules in astrobiology (Sorrell, 2001) and also of cometary matter, as in comet C/1995 O1 (Hale-Bopp) (Crovisier et al., 2004). CH_3COOH was first detected in a hot core source Sagittarius B2(N) (Sgr B2) (Mehring et al., 1997), and later also toward W51e2 (Remijan et al., 2002). It is considered the precursor to the simplest amino acid glycine (Dyson, 1999). HCOOCH_3 is ubiquitous in the ISM and has been observed not only in hot cores like Sgr B2, but also in molecular clouds such as OMC-1. Relative abundance with respect to CH_3COOH is 20–100 in Sgr B2 and W51e2 (Mehring et al., 1997). The recent identification of HOCH_2CHO in Sgr B2 is a significant milestone from an astrobiological viewpoint. Glycolaldehyde represents the first member of monosaccharide sugar – a hydroxylaldehyde diose – and denotes an important biomarker that can react to HOCH_2CHO phosphates (Krishnamurthy et al., 1999) and complex sugars such as ribose. The latter is the building block of ribonucleic acid, which carries genetic information in living organisms. Carbon hydrates such as HOCH_2CHO also play a role in vital chemical reactions (Weber, 1998). These species have been proposed to form on early Earth via the polymerization of two H_2CO molecules. Serious consideration has been given to the hypothesis that astrobiologically important molecules such as HOCH_2CHO could have been produced in extraterrestrial environments and were then introduced to Earth during the formation of the Solar System, possibly as a component of interstellar material or by comets during the period of heavy bombardment (Basiuk and Douda, 1999; Greenberg, 2002). Analysis of meteorites such as Murchison and Murray also indicates a large proportion of complex organic matter including sugars to support this claim (Dworkin et al., 2001). HCOOCH_3 was also identified via microwave spectroscopy in the coma of comet Hale-Bopp at intensities of 0.05 relative to water (Rodgers and Charnley, 2001); upper limits of CH_3COOH (0.06) and HOCH_2CHO (0.04) were provided too. CH_3COOH was detected tentatively via mass spectrometry in Halley. In the ISM, observations with millimeter arrays with improved spatial resolution show differences in the abundance of these isomers in distinct environments (Remijan et al., 2005) indicating that local

physical and chemical conditions influence the selective production of complex, astrobiologically important molecules. This shows the importance of correlating laboratory experiments with astronomical observations.

Recent theoretical and experimental work on ion–molecule reactions has shown quite clearly that gas-phase reactions cannot account for the presence of molecules readily found in ISM environments, such as HCOOCH_3 and even its precursors methanol, H_2CO , and others. Specifically, models based on pure gas-phase chemistry focusing on ion–molecule reactions of, for instance, methanol and H_2CO (Herbst, 1995) yield a factor of 50–100 less than observed (Lee et al., 1996). Mehringer et al. (1997) suggested an alternative to gas-phase reactions. As the velocity of CH_3COOH in the ISM of SgrB2 is close to ethanol and dimethylester, species that are thought to be synthesized on interstellar grains, these molecules are implied to be cospatial. They have been proposed to form via grain-surface reactions (Hasagawa and Herbst, 1993) in cold molecular clouds (van Dishoek, 1998) through radical–radical reactions on interstellar grains-sub-micrometer-sized silicate – and carbonaceous-based particles – and then to be liberated into the gas-phase via sublimation in hot cores when the surrounding matter is heated by the embedded protostar (Millar and Hatchell, 1998; Charnley et al., 2001). Millar and colleagues extended previous reaction networks and injected various saturated molecules from ices into the gas phase to simulate these grain sublimation processes (Charnley et al., 1992; Millar and Hatchell, 1998). However, even those refined models, while fitting observed abundances of complex molecules, still strongly underestimate their number densities. Garrod et al. (2007) used a coupled gas-surface model to show that species such as dimethyl ether, HCOOCH_3 and formic acid observed in hot cores are not made following sudden evaporation of methanol in the gas phase, but during a slow warming of ices coating grains. Yet, this statement is more about the inability of gas-phase reactions to explain the presence of these molecules than about knowledge of rates, kinetics, and energetics of species being formed on ices/grains. This reveals that key routes to form these $\text{C}_2\text{H}_4\text{O}_2$ isomers and complex organic molecules like carbon hydrates on interstellar grain material are still unknown.

The crucial role of grains and grain mantles in producing H_2 and simple hydrides such as water, ammonia, and methane has been recognized explicitly (Cazaux and Tielens, 2002). Roser et al. (2001) showed that oxidation of CO by O atoms in ices is a viable route to the formation of CO_2 in quiescent clouds, where solid CO_2 has been observed without the intervention of charged particles. The chemistry of CO is very important in the formation of complex organic molecules in ISM environments but no consensus has been reached whether molecules such as the $\text{C}_2\text{H}_4\text{O}_2$ isomers

can actually be formed on grain surfaces or inside icy grains. Ices, with thickness up to a few tens of nanometers, consist predominantly of H_2O , CH_3OH , CO, CO_2 , and of minor components like NH_3 , H_2CO , HCN, carbonyl sulfide (OCS), and CH_4 (Fraser et al., 2002; Ehrenfreund and Schutte, 2000). Chemical evolution of extraterrestrial ices and formation of new molecules by UV photons (Allamandola et al., 1999; Ehrenfreund et al., 2001; Gerakines et al., 2001, 1996) and cosmic ray bombardment have been well established (Hudson and Moore, 1999). Data from the Infrared Space Observatory suggest that deep inside photon-shielded molecular clouds such as Barnard 68 (B68), ices are processed predominantly through either charged particles of the galactic cosmic radiation field consisting of about 98% protons (p , H^+) and 2% helium nuclei (α -particles, He^{2+}) at a distribution maximum of a few MeV (Madey et al., 2003; Baragiola, 2003) or by neutral particles, predominantly atomic H (Barker and Auerbach, 1984; Zhdanov, 2000).

Therefore, to understand fully the formation of the $\text{C}_2\text{H}_4\text{O}_2$ isomers CH_3COOH , HCOOCH_3 , and HCOCH_2OH on and inside extraterrestrial ices, and to quantitatively pin down their role as evolutionary tracers in astrobiology, it is imperative to conduct systematic laboratory experiments on how these isomers are formed in extraterrestrial ices. These studies mimic the astrobiological evolution of distinct interstellar and Solar System environments both chemically (chemical composition of the ices) and physically (temperature, radiation exposure). The ultimate goal of these experiments is to provide reaction mechanisms and production rates of CH_3COOH , HCOOCH_3 , and HCOCH_2OH first in model ices and then in water-rich, realistic astrophysically relevant ices.

2.2.1. The retro-synthesis of $\text{C}_2\text{H}_4\text{O}_2$ isomers

To guide the selection of the ice mixtures, it is customary to conduct a retro-synthetic analysis of CH_3COOH , HCOOCH_3 , and HCOCH_2OH . In this method, chemical structures of the $\text{C}_2\text{H}_4\text{O}_2$ isomers are related to the structure of simple molecules detected on interstellar ices, including H_2O , CO, CO_2 , CH_3OH , H_2CO , CH_4 , NH_3 , and COS (Allamandola et al., 1999). Using this approach Bennett and Kaiser (2007a, b) and Bennett et al. (2007) determined that (1) a binary model ice of CO/ CH_3OH leads to the formation of all three $\text{C}_2\text{H}_4\text{O}_2$ isomers, (2) the binary ice CO_2/CH_4 may form CH_3COOH and HCOOCH_3 , and (3) two H_2CO molecules can form HOCH_2CHO and HCOOCH_3 (Table 2). There are therefore three model ices that can form the three isomers.

2.2.2. Abundances of precursors in interstellar ices

The relative abundances of the precursor molecules listed in Table 2 allow us to evaluate the relative

Table 2. Model ices and predicted reaction products

Model ice	Acetic acid	Glycolaldehyde	Methyl formate
CO/CH ₃ OH	+	+	+
CH ₄ /CO ₂	+	–	+
H ₂ CO	–	+	+

importance of each of the systems to be investigated. Carbon monoxide is the second most abundant molecule condensed on dust grains in the ISM, after water. However, the solid-state CO abundance and distribution in different interstellar dust clouds is heavily dependent on the history and present conditions of the cloud. Temperature has a great effect on the proportion of solid vs. gaseous CO, which can range from <1 to 60%. After cataloging a number of interstellar sources, Chiar et al. (1998) found that there are three different types of interstellar dust clouds. The first has a higher fraction of CO in apolar ices with only a weak absorption for CO in polar ices and a total abundance of CO/H₂O of >25%. The second group usually has equal amounts of CO on apolar and polar grains where the percentage of CO/H₂O is 0–20%. The last group contains embedded objects where no CO was detected; CO appears to have been sublimed at elevated temperatures. For some young stellar objects (YSOs) in group II (W33A, Mon R2 IRS 2, ρ Oph-Elias 29, Elias 32, WL5, WL12), the non-polar interstellar dust grains can only be compositionally modeled using greater than 90% CO, meaning that there exist icy grains in some regions of the ISM containing almost pure CO.

Methanol has long been known to be a constituent of the icy mantle on interstellar grains; however, its abundance relative to water is highly variable. A survey of 23 infrared sources by Gibb et al. (2004) using the Infrared Space Observatory found large discrepancies in the methanol abundance derived, in particular, when the 3.53 μm (2828 cm^{-1} [C–H stretch]), and 3.95 μm (2531 cm^{-1} [C–H stretch]) bands were used. For the high mass YSO Orion BN, the 3.53 and 3.95 μm bands implied upper limits of 4% and 27%, respectively, relative to water. For the intermediate mass YSO AFGL 989, by contrast, the 3.53 μm band yielded an abundance of ~23%, whereas the 3.95 μm band yielded only ~2%. Despite these inconsistencies, a general trend between methanol abundance and the amount of energetic processing occurring within the astronomical environment was suggested. The ices in the line of sight from Elias 16 are thought to be in a quiescent environment from which a methanol abundance of only 3% was reported. On the other hand, the ices surrounding high mass YSOs have abundances as high as 15–30% relative to water.

Besides the abundant CO and methanol constituent, CO₂ and CH₄ have also been detected in interstellar ices,

but at much smaller abundances of <20% CO₂ and 1–4% CH₄ relative to water. H₂CO can be found at up to 10% (Boogert et al., 1996, 1997, 1998; Keane et al., 2001).

Based on relative abundances, CO/CH₃OH ices should have the highest probability to synthesize CH₃COOH, HOCH₂CHO, and HCOOCH₃ upon interaction with ionizing radiation, followed by CH₄/CO₂-bearing ices and H₂CO.

2.2.3. Water-rich astrophysical ice analogs

As water is the dominant component of interstellar and cometary ices (Allamandola et al., 1999), the effects of water admixture are critical. Water can influence the outcome of a chemical reaction in three ways:

- (1) Water can act as an energy transfer medium. All astrobiologically important C₂H₄O₂ isomers are formed via radical intermediates. In a gas, the recombination products are not stable due to internal energy gained from the formation of a new chemical bond in the radical–radical recombination. These initially formed reaction products will therefore break apart. In the solid state, however, the internal energy of each radical–radical recombination product can be transferred to the surrounding water matrix via phonon interaction. This is important in stabilizing the newly formed molecules in water-rich ice mantles.
- (2) The incorporation of water ice can dilute reaction centers. For a chemical reaction to produce the astrobiologically important molecule in the solid state, both radical reactants must be in close proximity, preferably as neighboring molecules. The radicals being considered are very complex and heavy. In strong contrast to light atoms such as atomic H, these radicals are immobile in ices at low temperature. By adding water, we can investigate to what extent it separates the reacting radicals in the ices. This will certainly have an effect on the absolute production rates of astrobiological molecules.
- (3) Water molecules can actively participate in ice chemistry. It is well known that water can undergo unimolecular decomposition upon exposure of water ices to ionizing radiation. The product yields depend strongly on the temperature and structure of the ice, i.e., crystalline vs. amorphous. Here, the primary decomposition products can react with the astrobiologically important radicals and molecules, thus reducing production rates.

2.2.4. Laboratory simulation setup

Bennett et al. (2004) carried out experiments in a contamination-free ultrahigh vacuum (UHV) chamber (Fig. 2). It consists of a 15 L stainless steel cylinder that can be evacuated to 5×10^{-11} Torr by a magnetically

suspended turbopump backed by an oil-free scroll pump. A two-stage closed cycle helium refrigerator – interfaced to a differentially pumped rotary feedthrough – is attached to the lid of the machine and holds a polished silver (111) single crystal. This crystal is cooled to 10.4 ± 0.3 K, serves as a substrate for the ice condensates, and conducts the heat generated from the impinging charged particles to the cold head. To minimize the radiative heat transfer from the chamber walls to the target, a 40 K aluminum radiation shield is connected to the second stage of the cold head and surrounds the crystal. Ice condensation is assisted by a precision leak valve. During the actual gas condensation, the deposition system can be moved in front of the silver target. This guarantees a reproducible thickness and composition of the frosts. To allow selection of the target temperature, a temperature sensor, cartridge heater, and programmable controller are interfaced to the target; any temperature between 10 and 350 K can be obtained. This allows simulation of low-temperature conditions in cold molecular clouds and of comets in the Oort cloud (10 K), as well as of sublimation in the hot molecular core stage (100–300 K) and in comets approaching perihelion (100–300 K).

Ices are condensed on the silver target by a baked gas deposition system. The thickness of the ice layers (a few tens of nanometers) can be determined via infrared spectroscopy. The surface temperature of the sample can be quantified during irradiation using a mass spectro-

meter in residual gas-analyzer mode. Accounting for composition, energy, and flux of the cosmic ray particles and the energy range of the generated secondary electrons, one second of charged particle irradiation simulates about 10^8 s in the ISM. Accounting for typical life time of cold molecular clouds of 10^5 – 10^6 years, the irradiation experiments have to be conducted for 1–10 h. Recall that the ultra-high vacuum conditions in the simulation chamber limit condensation of one monolayer of residual gases to 70 h; comparing these data with the actual experimental time of up to 10 h demonstrates the contamination-free conditions achieved with this apparatus.

Ices were irradiated isothermally with 5 keV electrons; typically, the experiments are first conducted at 10 K – the lowest temperature achievable – to limit any thermal effects. These results are compared with those obtained at higher temperatures to elucidate the role of non-equilibrium (suprathermal) chemistry, which is temperature independent, vs. traditional, thermal chemistry. To guarantee an identification of the reaction products in the ices and those subliming into the gas phase on line and in situ, two detection schemes are incorporated: a Fourier transform infrared spectrometer (FTIR), and a quadrupole mass spectrometer (QMS). The chemical modification of the ice targets is monitored during the experiments to extract time-dependent concentration profiles and hence production rates of newly formed molecules and radicals in the solid state. The latter are

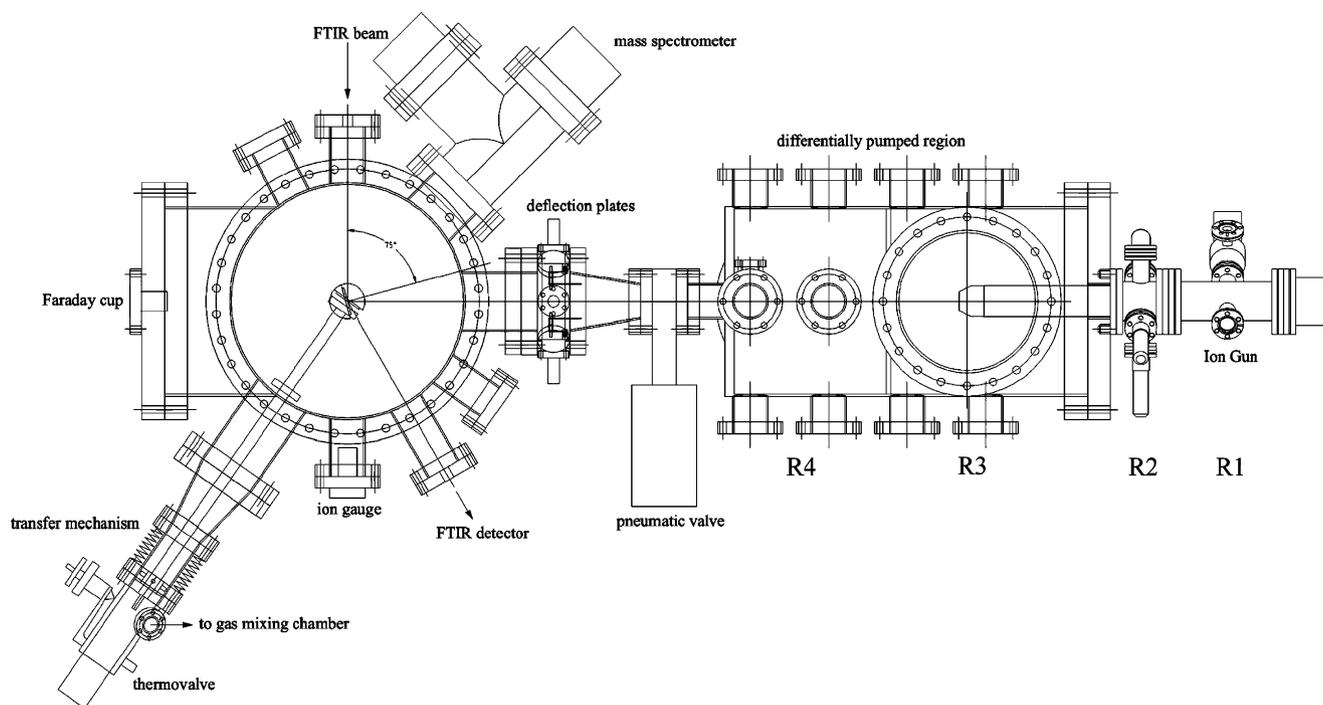


Fig. 2. Schematic top view of the simulation chamber, irradiation unit, quadrupole mass spectrometer (QMS), Fourier transform infrared (FTIR) spectrometer, and the gas condensation unit. The deflection plates fine-tune the center of the charged particle beam on the sample. The ion gun can be replaced by an electron source.

sampled via a Nicolet FTIR spectrometer (10,000–500 cm⁻¹) operating in an absorption–reflection–absorption mode; spectra are accumulated for 2.5 min at a resolution of 2 cm⁻¹. Since experiments are conducted for up to 10 h, one can therefore also follow the temporal evolution of the newly formed species. This gives additional information on the reaction mechanism. The infrared beam is coupled via a mirror flipper outside the spectrometer, passes through a differentially pumped potassium bromide window, is attenuated in the ice sample before and after reflection at a polished silver wafer, and exits the main chamber through a second differentially pumped KBr window before being monitored via a liquid nitrogen cooled detector (MCTB). The gas phase is monitored by a QMS (Balzer QMG 420) with electron impact ionization at 90 eV electron energy of the neutral molecules in the residual gas analyzer mode (1–200 amu). The raw data, i.e., the temporal development of the ion currents of distinct mass-to-charge ratios, are processed via matrix interval algebra to compute absolute partial pressures of the gas-phase molecules (Kaiser et al., 1995).

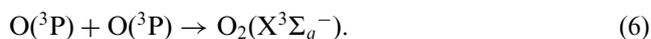
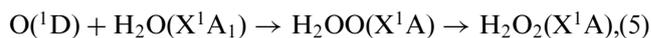
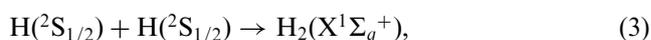
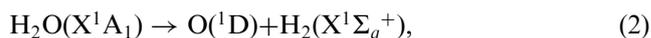
2.2.5. Experimental results

Experiments irradiating the ice mixtures in Table 2 at 10 K allowed construction of a quantitative, mechanistic model for the formation of three astrobiologically important biomarkers on and inside interstellar, water-rich ices: CH₃COOH, HCOOCH₃, and HCOCH₂OH (Bennett et al., 2006, 2007; Bennett and Kaiser, 2007a, b). The mixture of CO and methanol produced HCOOCH₃ and glycoaldehyde, whereas the mixture of CO₂ and methane produced only CH₃COOH. We also studied the effects of ionizing radiation on pure water samples at various temperatures between 10 and 150 K. Our ultimate goal is to investigate ternary mixtures of H₂O/CO/CH₃OH and H₂O/CH₄/CO₂.

As water ice is the main component of interstellar and cometary ices, Zheng et al. (2006a, b) investigated the formation of new molecules and of transient species (atoms, radicals) in pure water ices over a wide temperature range from 10 K to the sublimation of water. Mass spectrometer and FTIR data suggest the formation of H (OH as a by product), O, O₂, and H₂O₂. HO₂ radical and ozone (O₃) were not detected. The absolute production rates decreased as the temperature increased from 10 to 110 K. Also, a quantitative study of D₂-water indicated that the production rates of molecular deuterium, O₂ and D-hydrogen peroxide were systematically higher in amorphous ices than in crystalline ices (Zheng et al., 2007a, b).

A quantitative analysis of these data suggests that water can undergo unimolecular decomposition via reactions (1) and (2), thus forming atomic H plus the OH radical and electronically excited O atoms plus H₂, respectively. The H atoms can recombine to generate H₂

as well. Hydrogen peroxide was formed via two pathways, a recombination of two OH radicals as in reaction (4), and/or reaction of electronically charged O with water through an oxywater intermediate as in reaction (5). Note that O₂ can be formed via simple recombination of ground-state oxygen atoms relaxed from the electronically excited state as in reaction (6). It should be stressed that once oxygen is added to the water sample, additional reaction pathways can be opened such as the successive addition of two hydrogen atoms to molecular oxygen-forming hydrogen peroxide (Zheng et al., 2007a, b).



2.2.6. Summary and implications

We have conducted systematic laboratory studies on the formation of three C₂H₄O₂ isomers CH₃COOH, HCOOCH₃, and HCOCH₂OH on binary model ices of CO–methanol (mixture 1) and CO₂–CH₄ (mixture 2). These ices were selected based on a retro-synthetic approach and on the abundances of these molecules in the ISM. In mixture 1, we identified two isomers, HCOOCH₃, and HOCH₂CHO, whereas in mixture 2 only CH₃COOH was detected. Considering the chemical separation in distinct interstellar environments, our experiments suggest that the astronomically observed differentiation could result from distinct compositions of the processed icy grains. Considering the mechanism, both of the H-bearing precursor molecules, methane and methanol, undergo unimolecular decomposition to form a radical R plus a hydrogen atom. The latter has excess kinetic energy and therefore must be classified as suprathermal H. These species can add to triple and double bonds of molecules forming the HCO and HOCO radicals (R'), respectively. If the radical R and the oxygen-bearing radical R' are formed in neighboring sites and if they hold the correct orientation geometry, they may recombine to form the observed C₂H₄O₂ isomers. Otherwise, they sit isolated in the ice samples. This reaction sequence of (1) unimolecular decomposition forming a suprathermal H atom, (2) addition of the suprathermal H atom to a double or triple bond, and (3) a radical–radical recombination could represent a versatile reaction sequence to form astrobiologically

important molecules in extraterrestrial ices. Note that this sequence has also been observed in the formation of acetaldehyde and glycine together with its isomer (Holtom et al., 2005) in electron-irradiated interstellar analog ices.

These model ices contain only non-polar molecules. Therefore, these simulation experiments may mimic efficiently the chemical processing of non-polar astrophysical ices. However, polar, water-rich ices exist in the ISM too; they dictate as well the icy composition of comets. Since the irradiation of pure water ices verified the formation of reactive atoms (H, O) and radicals (OH), it is likely that the admixture of water to the ices changes the production routes and yields. For instance, the reaction intermediates to form the $C_2H_4O_2$ isomers are radicals. Here, H generated from the radiolysis of water can add to these radicals and form closed-shell molecules. Consequently, the radicals are no longer available for radical–radical recombination to synthesize the $C_2H_4O_2$ isomers. This will certainly reduce the yield; a “dilution” of the radical reaction centers by the water molecules may amplify this scenario. On the other hand, the suprathreshold H atoms generated in the unimolecular dissociation of water can also add to the CO and CO_2 molecules forming HCO and HOCO, respectively. Logically, this would actually enhance the formation of radicals crucial to the synthesis of CH_3COOH , $HCOOCH_3$, and $HCOCH_2OH$. In summary, the addition of water and the simulation of water-rich and polar astrophysically relevant ices is a complicated task. Experiments are currently underway to investigate these mixtures.

3. Water in the Solar System

3.1. Where did it come from?

Water in the ISM was present in the natal cloud that was the birthplace of our Solar System. It played a key role in the evolution of the cloud as it collapsed to form the protoplanetary disk out of which the planets grew. Until recently, models of the formation of the Solar System could be constrained only by the chemistry of remnant small bodies such as comets and asteroids. A new era dawned as we began to observe molecular lines directly on disk surfaces at sub-millimeter wavelengths, providing new insight into disk chemistry. As a protoplanetary disk collapses it has a flared structure, increasing in thickness with distance from the forming star. Chemically, the disk is vertically stratified into a photon-dominated surface layer, a warm molecular layer, and a midplane freeze-out layer which disappears as temperature increases radially inward (Bergin et al., 2007). For most of the disk midplane, temperatures are

very low and heavy molecular species are largely frozen out onto dust grains. As midplane temperatures increase, volatiles sublime at different radial distances depending on their sublimation temperature.

At temperatures below 180 K water is a stable solid. The so-called “snow line” beyond which water freezes out was likely near 3–5 AU in the Solar nebula (Boss, 1998), and it would have moved inward with time. As the nebula collapsed, the original icy mantles on interstellar grains were likely not preserved. The grains were probably heated as they fell into denser parts of the nebula toward the midplane, and the ices sublimated. These volatiles would later have recondensed onto other grains (Lunine et al., 1991). These icy grains strongly influenced the temperature structure of the disk because they influence the mean disk opacity. Likewise, freeze-out of icy grains in the disk can influence the transport of energy, mass, and angular momentum in the disk (Pollack et al., 1994; Ciesla and Cuzzi, 2006). Disk surface processes probably dominate the chemistry that can be observed, but it is not certain how much this chemistry interacts with that in the disk midplane. It is clear that at the low midplane temperatures D/H fractionation will proceed via ion–molecule reactions, and the D enrichment will propagate to other species such as water. It is expected that within the disk there will be a strong variation of D/H with temperature, i.e., with radial distance and height in the disk. Gas-phase reactions can be important too; for molecules of lower volatility such as water, however, gas-phase interaction is less likely in the cold outer nebula (Bergin et al., 2007). Until disk chemistry is fully understood, it is dangerous to make direct connections between the state of precursor interstellar materials and the remnants of Solar System formation we see today in the small Solar System bodies.

Dynamical models of small body evolution and accretion and growth of planetesimals are refining understanding of the early Solar System. Weidenschilling (1997) has shown that planetesimals grow by collisional coagulation until they are big enough to decouple from the turbulence between the particle layer and the gas. This decoupling occurs when planetesimals are ~10–100’s of meters in size. Depending on the timescales of formation, there could have been significant radial mixing, bringing planetesimals of different chemistries together in the same bodies. Dust grains can also undergo substantial radial mixing in the protoplanetary disk due to turbulence, gas drag and viscous evolution (Ciesla, 2007). Dynamical and chemical evidence suggests that comets had source regions in the low-temperature regions of the outer Solar System, forming in the giant-planet region out to the Kuiper belt (Mumma et al., 2002, Bockelee-Morvan et al., 2004). Comets can get perturbed inward from the Oort cloud by stellar encounters and the galactic tidal field

(and molecular clouds) and inward from the Kuiper belt region by perturbations from the giant planets, especially Neptune.

3.2. Observable water in the solar system

Water is the most abundant condensable volatile molecule in the Solar System. Water ice is found in a wide range of small Solar System bodies from the main asteroid belt outward and there is mineralogical evidence for significant aqueous alteration within asteroids of the main belt. Astronomically, water and hydrated minerals are primarily detected through absorption bands in the near-infrared at 1.5, 2.0, and 3.0 μm . This latter band is difficult to observe from the ground because of strong absorption in the terrestrial atmosphere.

Chondritic meteorites (chondrites) are fragments of mineralogically and chemically diverse asteroids that formed at 2–3 AU from the Sun concurrently with (and even after the early stages of) the accretion of the planets in the inner Solar System (Mercury, Venus, Earth, Mars). Asteroids, like planets, formed by aggregation of solids and gas from the protoSolar disk. Remote sensing of asteroids and laboratory studies of chondrites show that asteroids at 2 AU largely consist of anhydrous silicates, metal, and sulfides, whereas at distances >3 AU most asteroids are composed of hydrated silicates such as clay minerals, organic matter, carbonates, sulfates, magnetite, and other iron oxides. Some of the hydration could have occurred by gas-phase reactions, but most is attributed to alteration by liquid water inside the parent asteroids (McSween, 1979; Zolensky et al., 1989; Brearley, 2004). Chondrites are not particularly good analogs for the building blocks of the Earth since no combination of known chondrites can reproduce Earth's chemical and isotopic makeup (Burbine and O'Brien, 2004).

To date more than 160 natural satellites have been discovered orbiting planets in our Solar System. These moons represent a wide diversity of physical and chemical compositions, ranging from planetary-sized bodies with complex thermal histories and geological activity to mere collisional debris. The compositions of the satellites have been constrained by remote sensing (visible and near-infrared imaging reflectance spectroscopy) and thermal and radar measurements. The surfaces of the outer Solar System satellites are rich in ices, combined with refractory materials and a rich suite of organic materials.

Beyond the realm of the gas-giant planets, asteroids, and satellites, the outer Solar System is populated by the Trans-Neptunian Objects and their subclass, the Centaurs (which are TNOs that are evolving dynamically inward, crossing the orbits of the giant planets, and

which will eventually be visible as comets). Over 1200 of these objects have been discovered to date. They exhibit a wide diversity in colors and surface composition, with some showing diagnostic spectral bands of water ice, methane, and nitrogen, and others showing no absorption features. The large range of apparent surface compositions may reflect heterogeneity in the bulk starting compositions, or different surface evolutionary processes. The reflectance properties of a surface that is composed of an intimate mixture of dark and light, high-albedo material will be dominated by the spectral properties of the dark material (Hapke, 1981). Whatever the explanation for the diversity, it is clear that water is a major component of surfaces in the outer Solar System.

For a long time, the water-rich nuclei of comets were suspected as major carriers of water to the terrestrial planets. Measurements of the D/H ratio in comets P/Halley, C/Hyakutake and C/Hale-Bopp have indicated a problem with the simplest version of this idea, however. The D/H ratio in these comets averages 310×10^{-6} , which is twice the value for Earth's oceans of 156×10^{-6} (Table 1). The three measured comets are from dynamical classes thought to derive from the Oort Cloud, and to have originated in the middle Solar System. The comets in the Kuiper Belt (so-called short-period, Jupiter-family comets) remain unmeasured. Other possible problems with a cometary source for the bulk of Earth's water are that they may introduce too much of the noble gases and their collision probabilities are too low, one in a million for a typical comet during its dynamical lifetime (Levison et al., 2001).

Water was first measured in comets in the 1970s from observations of H and OH. It was directly measured for the first time in comet Halley, from the Kuiper Airborne observatory and from space (Mumma et al., 1986; Combes et al., 1988). The presence of water is also inferred when small bodies such as comets approach the Sun closely enough that water ice sublimates and becomes detectable. Understanding how water is observed is key to understanding its distribution and state within our Solar System.

A new class of objects has recently been discovered in the main asteroid belt: the Main Belt Comets (Hsieh and Jewitt, 2006). To date, three objects have been found that exhibit cometary activity in the main belt. They have colors and sizes typical of comet nuclei, but their activity levels are quite low compared to active comets. Nevertheless, activity persists for months and is correlated with perihelion passage, and so is consistent with dust ejection from the surface driven by water-ice sublimation (Hsieh, 2007). Thermal models show that it is possible for high-porosity, low-density comet nuclei to preserve ice over the age of the Solar System, but only if the ice is buried beneath the surface. These objects occupy orbits in the main belt that are indistinguishable

from those of the asteroids. Dynamical simulations suggest that they are not comets that have been captured from farther out in the Solar System (Fernandez et al., 2002), but are more likely icy bodies that have been stored at their present location over the age of the Solar System. Statistics suggest there could be thousands of Main Belt Comets within the asteroid belt. As such they represent a new reservoir of icy planetesimals that could have delivered water to the primordial Earth.

Two recent space missions to comets provided interesting insights into the water story. The Stardust mission flew through the dust/gas cloud (coma) of comet 81P/Wild 2, a typical Jupiter-family comet, and returned to Earth with samples of comet dust. In 2005, the Deep Impact mission flew two spacecraft to comet 9P/Tempel 1 and impacted the comet at 10.3 km/s, excavating dust and volatiles that were observed from space (A'Hearn et al., 2005) and observatories on Earth (Meech et al., 2005). Both missions returned significant results that bear on cometary composition, origin, and their relevance for water delivery to Earth. Of particular interest is that the dust from both missions showed strong evidence that it had been thoroughly mixed in the proto-Solar nebula prior to its incorporation into the comets (Lisse et al., 2006; Brownlee et al., 2006; Zolensky et al., 2006). Remote spectra and laboratory analysis of the grains show that they consist of a mixture of materials, including high-temperature refractory, aqueous processed, and low-temperature material. Most of the cometary material had been widely circulated and processed in the nebula. This suggests that interpreting the role of comets in the delivery of water to Earth based on their isotopic signatures is premature: there is a complex history of formation conditions and dynamical and physical evolution that needs to be understood first. Of the handful of comets for which we have detailed in-situ chemical and physical information, each one so far is completely different.

Water ice that formed under conditions of low-pressure vapor deposition expected in the Solar nebula can condense into four different forms: two crystalline polymorphic forms and a low- and high-density amorphous form. When water ice condenses at temperatures below 100 K it condenses in the amorphous form because it lacks the energy to form a regular crystalline structure. During condensation in the amorphous form it can trap gases in concentrations as high as 3.3–3.5 times the amount of the ice. The amount of trapped gas is extremely sensitive to the temperature of condensation. When amorphous water-ice is heated, small amounts of trapped gases are released between 35 and 120 K in response to restructuring of the ices in a process called annealing (Bar-Nun and Laufer, 2003). Beginning near 90 K, gases are released as the ice undergoes an exothermic amorphous-to-crystalline phase transition. Thus, gases will be released from

water over a range of distances from the Sun. The primary driver for comet activity close to the Sun is water sublimation ($T \sim 180$ K). Early models attempting to explain the presence of highly volatile compounds with orders of magnitude differences in vapor pressure appearing nearly simultaneously in the cometary comae invoked the idea that these compounds were trapped as clathrate hydrates. Clathrate formation in impure ices is unlikely; laboratory experiments demonstrate that clathrate formation for many species is impossible at low temperature and pressure, and their presence is not necessary to explain the presence of species other than water (Jenniskens and Blake, 1996).

4. Water on earth

The problem of the origin of H₂O on Earth and its distribution and history has remained one of the most intractable problems in geochemistry, because it is inextricably bound to three equally difficult problems: the origin of the Earth; its chemical differentiation into core, mantle, and crust; and the heterogeneity of its mantle (Martin et al., 2006).

The pioneering calculations of Safranov (1969) and Wetherill (1985) on orbital evolution and the dynamics of planetary accretion first showed that planets such as Earth were probably assembled stepwise. Rather than growing by gradual accretion of small fragments to a much larger body, it is now thought that the final assembly of Earth and Venus took place catastrophically, by sequential collision of a few dozen Moon- to Mars-sized planetary embryos (Canup and Righter, 2000; Chambers, 2004) which themselves had assembled by runaway growth within only a million years after the Solar nebula began to condense (Yang et al., 2007), 4.567 billion years ago (Ga) (Amelin et al., 2002). Earth was assembled in this violent fashion over a period probably no longer than 30–50 Myr following the onset of nebular condensation, based on Hf-W isotopic evidence that Earth's core had formed by this time (Schoenberg et al., 2002; Yin et al., 2002; Kleine et al., 2002; Jacobsen, 2005; Halliday and Kleine, 2006; Halliday, 2006). The final episode in core formation is believed to be the giant impact that formed the Moon, by which Earth gained the last 10% of its mass in collision with a Mars-sized body that has been named Theia (Canup and Asphaug, 2001; Canup, 2004; Kleine et al., 2005).

This new scenario has important implications for the origin and history of H₂O on Earth because (1) modeling indicates that embryos that collided to form Earth could have come from considerable radial distances within the inner Solar System and thus may have contained widely variable amounts of water and other volatiles (Morbidelli et al., 2000; Raymond et al.,

2004); (2) the energy released on impact of these sizeable embryos would have shattered and probably vaporized them, releasing their volatiles instantaneously by impact degassing (Lange and Ahrens, 1982); (3) impacts as large as that which formed the Moon would have melted much of Earth, forming a deep magma ocean in which vaporized volatiles could have dissolved; and (4) such large impacts would have blasted into space a substantial fraction of Earth's then complement of volatiles, including H₂O (Genda and Abe, 2005). The result is that both Earth's initial volatile content and the amount it retained become highly uncertain and subject to the vagaries of the accretion process. The history of water on Earth also switches from the traditional tale of outgassing of volatiles from Earth's interior over time via volcanism, to one dominated by ingassing of H₂O and possibly other volatiles that were originally deposited mainly at Earth's surface (Kasting and Catling, 2003). Ingassing of water ultimately lubricated Earth's mantle sufficiently that, even after it had solidified, it could continue to cool by convection, thus producing plate tectonics. Melting of a wet mantle also produced continental crust, creating land that would rise above the oceans where life would originate.

Earth's hydrosphere is estimated to contain 1.6×10^{21} kg H₂O, and its exosphere, which includes the crust, 1.9×10^{21} kg H₂O (Table 3). Whether this represents most of the H₂O (or more correctly H) on the planet or only a small fraction is uncertain, as the amount in the mantle and especially the core is poorly known. Current estimates range from 0.1 to 1.5 additional hydrospheres in the mantle and up to 100 in the core, although actual amounts in the core could be much smaller than this, even zero (Williams and Hemley, 2001; Hirschmann, 2006). As with other highly volatile species in Earth's exosphere including C, N, and the noble gases, the wide range in the estimates results from our imperfect understanding of how Earth acquired its volatiles and what happened to them subsequently.

4.1. How earth got its water

There are several mechanisms by which Earth could have acquired its water, and it seems likely that all of them have contributed to some extent: (1) accretion of water as a component of the planetary embryos that accreted to form Earth ("wet" accretion); (2) acquisition of H and water directly from the Solar nebula, by adsorption onto accreting materials and by dissolution into a magma ocean; and (3) late impact of especially wet bodies such as carbonaceous chondrites and comets. Once water reached Earth it was susceptible to loss by physically induced impact erosion and thermally induced hydrodynamic escape, in which the major gases

are lost to space, dragging minor gases with them, and Jeans escape, in which only the lightest, highest-velocity molecules are lost. Water was also incorporated into the forming planet, by dissolution into a magma ocean, burial, and ultimately subduction. Water was mixed into the mantle and crust and then recycled by plate tectonics and outgassed by volcanism. Each of these mechanisms brought in and processed C, N, and noble gases as well as water. A satisfactory model for the origin of Earth's oceans and atmosphere would produce the proper proportions of the various volatile species and explain their distribution among the core, mantle, crust, atmosphere, and oceans.

Numerical models that replicate planetary accretion in the inner Solar System (Morbidelli et al., 2000; Chambers, 2004; Raymond et al., 2004), from Mercury at 0.4 AU to Mars at 1.5 AU, have four results in common that are highly significant for Earth's chemical composition: (1) about half the mass of Earth-sized planets that form near Earth's location at 1 AU accretes from planetesimals and planetary embryos that formed locally; (2) the other half accumulates from embryos scattered from more distant regions, both closer to the Sun and farther away, from ~0.4 to 5 AU (Jupiter is now at 5.2 AU), and including the asteroid belt, mainly between 1.9 and 3.2 AU; (3) the embryos from farther away, including the presumably wetter ones from the outer asteroid belt, tend to arrive later, during accretion of the second half of the planetary mass; and (4) final assembly of the terrestrial planets from planetary embryos takes 10–100 Myr, the same duration indicated for Earth's formation from the Hf-W isotopic data. Accretion of Earth mainly from locally condensed and accreted materials is consistent with the conclusion that its composition, including its major as well as its trace elements and isotopes, is significantly different from that of the Sun and every known class of meteorite, or any other extraterrestrial material. As noted by Drake and Righter (2002) and Righter et al. (2006), the building blocks of Earth are at present unsampled. Presumably, the unique material that condensed and accreted near 1 AU, in Earth's "feeding zone", was all swept up into the growing Earth, whereas the vast majority of meteorite parent bodies (except perhaps those of iron meteorites) accreted farther from the Sun, in the asteroid belt, and so acquired a different bulk composition from Earth.

4.1.1. "Wet" vs. "dry" accretion

Earth, like all known Solar System materials, is depleted in volatile elements relative to the Sun. The cause of this depletion, by partial condensation or partial evaporation, is still debated (Davis, 2006), but the observation that all known materials are depleted implies that depletion occurred early and throughout the inner Solar System (Palme and Jones, 2004; Palme and

Table 3. Mass of water on Earth and relevant deuterium contents

	Mass of H ₂ O (10 ¹⁸ kg)	H ₂ O wt% or ppm	As ppm H in BSE ^a	δD (‰) VSMOW	δD ±(‰)	D/H (10 ⁻⁶)	Ref.
Oceans	1371.3		38	0		156	1
Marine sediment porewater	180		5	-1		156	2
Marine basement formation water	26		0.7	-1		156	3
Ice	27.8		0.8	-350	50	101	1
Continental groundwater	15.3		0.4	-10		154	4
Lakes, rivers, soils	0.192		0.01	-10		154	4
Total hydrosphere	1621		44	-6		155	
		wt%					
Shales	221	15	6	-80	20	143	5
Continental carbonates	2.56	1	0.1	-60	20	146	5
Evaporites	0.42	1	0.01	-5	15	155	5
Marine clays	7.56	15	0.2	-50	20	148	5
Marine carbonates	0.504	1	0.01	-30	10	151	5
Total sedimentary rocks	232		6	-79	20	144	5
Organic matter	1.36	85	0.04	-100	30	140	5
Continental metamorphic rocks	36	1.5	1.0	-80	20	143	5
Oceanic (igneous) crust	41	0.7	1.1				6
Total exosphere	1931		53	-17		153	2
Mantle							
Serpentinite in oceanic lithosphere							
Low estimate	11		0.3				7
High estimate	27		0.7				2
Upper mantle		ppm					
To 410 km	74	120	2				2
410–670 km (low est)	56	120	2				2
410–670 km (high est)	930	2000	26				2
Lower mantle							
Low estimate	59	20	2				8
LM except D''	56	20	2				8
D'' only (H ₂ O rich)	83	500	2				2
LM + D'' (H ₂ O rich) (mid-est)	140	20, 500	4				2
High estimate	1470	500	40				2
Total mantle							
Low estimate	200		5				2
Mid estimate	280		8				2
High estimate	2500		69				2
		Bulk silicate Earth:					
Total Earth (except core)		ppm H₂O	ppm H				
Low estimate	2130	526	58				2
Mid estimate	2210	546	61				2
High estimate	4430	1095	122				2
High est. of Lecuyer et al. (1998)	5000	1236	137				5

^aBSE = Bulk Silicate Earth. Estimate for serpentinite in the oceanic lithosphere includes slow-spreading ridges, outer forearc highs, and subducted slabs. Mid-estimates use low estimate for upper mantle and assume 500 ppm H₂O in 200-km thick D'' layer and 20 ppm elsewhere in lower mantle. Refs.: (1) Hay et al. (2006), (2) this paper, (3) Johnson and Pruis (2003), (4) Berner and Berner (1996), (5) Lecuyer et al. (1998), (6) Rupke et al. (2004), (7) Lee and Chen (2007), (8) Hirschmann (2006).

O'Neill, 2005). Early depletion of the moderately volatile element Mn is likewise indicated by Mn–Cr isotope systematics in the inner Solar System (Lugmair and Shukolyukov, 1998). As the most volatile elements are the most depleted, Earth is most deficient in He, Ne, Ar, Xe, Kr, H, N, and C, in that order. Earth is depleted to a lesser extent in all other volatile elements, from B and O through Pb and Bi. For 28 of 30 refractory lithophile elements, by contrast (the exceptions are V and Nb, which have presumably partitioned somewhat into Earth's core, along with the refractory siderophile elements), Earth has elemental ratios nearly identical to those of chondritic meteorites; likewise, the ratios of these 30 elements are similar in all classes of chondritic meteorites, within $\leq 5\%$. Among the meteorite classes, Earth most closely resembles the carbonaceous (C-) chondrites, especially in its major-element composition. Allegre et al. (2001) showed that Earth most closely resembles CI-chondrites in its Fe content and refractory element composition, and CM-chondrites in its moderately refractory elements. For the volatile elements, however, including the alkalis and halogens, Earth is more depleted than the CV-chondrites, the most depleted class of C-chondrites. The highly volatile elements follow this pattern as well. According to our best estimate of Earth's water content (Table 3), Earth contains 60–120 ppm H, or 0.05–0.11 wt% H_2O , when all water in the hydrosphere, crust, and mantle is divided into the mass of the Bulk Silicate Earth (BSE = mantle + crust) of 4.05×10^{27} g. This is 5–50 times less than the two driest classes of C-chondrite, the CV's (2.5 wt% H_2O) and CO's (0.63 wt%) (Wasson and Kallemeyn, 1988). Earth is even more depleted in C ($\times 50$) and N ($\times 70$) relative to these meteorite classes than it is in H_2O . Thus, even though Earth is often considered to have accreted "dry" such that the oceans could not have originated as part of the main accretion process, Earth is in fact quite dry even with its oceans, and it is conceivable that enough water was delivered by materials from Earth's local feeding zone near 1 AU to provide Earth with its trace amount of water. This prospect has been explored by Drake (2005), who concluded that enough water could have been adsorbed onto grains from Solar nebular gas to supply up to three oceans to the growing Earth. As he noted, however, such minimal supply does not provide much excess to allow for later losses during planetesimal formation and differentiation or as a result of giant impacts.

4.1.2. Ingassing from the solar nebula

Solar nebular gas, comprising mainly H_2 , He, H_2O , and CO, originally represented $>99\%$ of the mass of the Solar nebula. This gas would have been abundantly available to supply volatiles to the growing Earth only for the first few million years after the nebula began to

condense. As a star forms it first attracts this gas, and then drives away the remnant by intense T-Tauri stage ultraviolet luminosity and extreme winds. At the same time gravitational infall of gas from farther out can be intercepted by accretion onto giant planets such as Jupiter, which would have prevented it from reaching the inner Solar System once these giant planets began to form (Kallenbach et al., 2003; Montmerle et al., 2006a). Observations of young stars in star-forming regions of the galaxy indicate that dust is removed within a few million years, and presumably gas along with it, although this is much more difficult to observe (Hartmann, 2000). Disk lifetimes are typically 3–5 Myr, although in rare cases they can survive for 10 Myr (Russell et al., 2006). Dissipation of the Solar nebula within 3–5 Myr is consistent with the duration of chondrule formation in meteorites (Bizarro et al., 2004; Russell et al., 2006). Mars probably formed and differentiated its core within the first million years (Halliday and Kleine, 2006) (although Foley et al. (2005) estimate 12 Myr). Given that planetary embryos should form faster closer to the Sun (Kokubo and Ida, 2002), it is highly likely that Earth achieved the 10% of its final mass necessary to gravitationally capture nebular gases well within the lifetime of the Solar nebula. A primary atmosphere for early Earth derived directly from the Solar nebula then becomes inevitable (Harper and Jacobsen, 1996). The blanketing effect of this early atmosphere would have raised the surface temperature enough to melt the planetary surface, and to keep it molten had it already melted from the energy of large impacts (Sasaki, 1999).

Isotopic evidence for a Solar component in Earth's mantle is now unequivocal. On Earth, ^3He is a primordial isotope whereas ^4He is radiogenic, mainly from decay of U and Th. A component that feeds mantle plumes beneath oceanic islands is characterized by $^3\text{He}/^4\text{He}$ ratios $\sim 40\times$ that in the atmosphere, compared with the shallow (upper mantle) source of mid-ocean ridge basalts (MORB) of $\sim 8\times$ atmospheric (Graham, 2002; Hilton and Porcelli, 2005). The Solar nebular ratio, as measured in Jupiter's atmosphere, is $120\times$ that in Earth's atmosphere, and the present-day Solar wind is $330\times$ atmospheric, higher now than the ancient nebular value preserved on Jupiter because ^3He is continuously produced in the Sun by deuterium burning. As He is too light to be retained by Earth at its present mass, and so is continually lost to space by Jeans escape, it is significant that a reservoir of ^3He still resides within Earth's interior, stored there since Earth's formation. There are two such reservoirs, moreover, one (the plume source) more primitive than the other (the MORB source).

This same plume source that forms oceanic island basalts (OIB) has Solar Ne isotopic ratios for both $^{20}\text{Ne}/^{22}\text{Ne}$ and $^{21}\text{Ne}/^{22}\text{Ne}$ (Honda et al., 1993). Solar Ne

is evident in both MORB and OIB, but it is found in its purest form only in OIB, as the MORB source in Earth's upper mantle has higher $^{21}\text{Ne}/^{22}\text{Ne}$ from production of nucleogenic ^{21}Ne (along with ^4He) by U and Th decay via the “Wetherill reactions”, mainly $^{18}\text{O} + \alpha = ^{21}\text{Ne} + n$. The highest $^{20}\text{Ne}/^{22}\text{Ne}$ ratio measured in OIB from Iceland (13.3; Dixon et al., 2000; Moreira et al., 2001) and from a Devonian carbonatite in an ancient plume setting on the Kola Peninsula, Russia (≥ 13.0 ; Yokochi and Marty, 2004, 2005) is nearly as high as the Solar value of 13.8, and is significantly higher than that of (1) meteoritic Ne–B of ~ 12.5 , a mixture of Ne from the Solar wind (13.8) and Solar energetic particles (11.2); (2) the meteoritic Q-component of ~ 11.7 , the most abundant component in meteorites; (3) Ne in CI-chondrites, the class closest to Solar in its elemental abundances, of ~ 8.9 ; and (4) Earth's atmospheric Ne of 9.8 (Podosek, 2004). Ne in Earth's air can thus be interpreted as either meteoritic in origin, or Solar but highly fractionated, with preferential loss of the light isotope ^{20}Ne , in contrast with Ne in Earth's mantle, which is clearly Solar in origin. The large isotopic difference between air Ne and mantle Ne indicates that Earth must have outgassed its Ne early, and that the Ne contribution from the mantle has been insignificant since then. This is not unlikely considering that at least 75% and more likely 99% of Earth's Ne is presently in the atmosphere. The Solar Ne in Earth's mantle is a small remnant that records an important early episode in the history of Earth's volatiles, but is volumetrically insignificant compared with the much more abundant and very different Ne in the atmosphere.

Given the evidence for massive ($>99\%$) loss of Earth's early atmosphere, discussed below, it is unlikely that the Solar noble gases in the OIB (plume) source could have been delivered to Earth in sufficient quantities by the Solar wind, either directly or by implantation onto accreting planetesimals. Nor does the elemental abundance pattern of the noble gases in the mantle match that implanted in meteorites by the Solar wind (Harper and Jacobsen, 1996). In particular, the $^3\text{He}/^{22}\text{Ne}$ ratio of 7.7 is much higher than the Solar value of 1.9 (Honda and Macdougall, 1998). Whereas grains should absorb relatively more Ne than He, the solubility of He in a silicate melt is much greater than that of Ne. Thus the only mechanism that seems capable of providing noble gases in the OIB source is dissolution into a magma ocean. Sasaki (1999) estimated that Earth would have to acquire 40–60% of its final mass while still immersed in Solar nebular gas, to produce an atmosphere thick enough to supply the necessary amounts. For comparison, if the final episode of core formation resulted from a Moon-forming giant impact at 30 Myr (Jacobsen, 2005), then Earth would likely already have gained nearly two-thirds of its mass by 11 Myr (Yin et al., 2002). That Earth could have gained

mass fast enough to acquire a thick-enough Solar nebular atmosphere is thus possible, but not inevitable.

Neon isotopically similar to that in the MORB (upper mantle) source has also been found in continental well gases of magmatic origin in New Mexico and South Australia. It closely resembles the Ne–B component in meteorites. Ballentine et al. (2005) argue that this Ne is characteristic of Earth's “convecting mantle” (as opposed to the OIB/plume source) and that it was supplied mainly by the Solar wind impacting on planetesimals. There seems no doubt that Solar Ne was supplied to Earth both directly from nebular gases and indirectly by the Solar wind. Whereas well-gas Ne resembles MORB Ne, however, the Xe in the two sample types is isotopically distinct, in a manner that bears significantly on the origin of Earth's water, as discussed below.

As nebular gas was mainly H_2 , He, H_2O , and CO, it would have created appropriately reducing conditions for Fe metal to segregate into Earth's core. Prior to dissipation of the nebula, the nearly infinite supply of H_2 would have dominated, possibly reducing some of the FeO component in the silicate melt to Fe and creating even more water via the reaction $\text{FeO}_{\text{sil}} + \text{H}_2 = \text{Fe} + \text{H}_2\text{O}$. After the nebula had dissipated, the mass of Earth would dominate, and as Fe continued to sink to the core the mantle would become more oxidized. Hydrogen would dissolve readily into molten Fe at high pressure (Abe et al., 2000). If this scenario is correct, then Earth should contain substantial H in its core, estimated at up to 100 oceans worth (Williams and Hemley, 2001; Porcelli and Halliday, 2001). The identity of the light element(s) in the inner and outer core, required to explain their density, is a major unsolved problem (McDonough, 2005; Asahara et al., 2007; Badro et al., 2007; Corgne et al., 2007). Besides H, the leading candidates are O, Si, S, and C. Equally significant is the nature of the 200-km thick layer that surrounds the core known as the D'' layer (Boyet and Carlson, 2005; Brandon and Walker, 2005; Tolstikhin and Hofmann, 2005; Murakami et al., 2007).

4.1.3. Late impact of wet planetesimals or comets

As noted, Earth was more likely to accrete planetary embryos from farther away during the second half its accretion, including ~ 10 –25% from beyond 1.5 AU and some wetter ones from the outer asteroid belt at 2.5–3.5 AU (Morbidelli et al., 2000; Chambers, 2004; Raymond et al., 2004). As the various classes of C-chondrites contain between 0.6 and 19 wt% H_2O (Wasson and Kallemeyn, 1988), ~ 5 –400 times more than the Bulk Silicate Earth (Table 3), a contribution of only a few percent from C-chondrites could supply Earth's water in excess. Comets, much more volatile-rich than even C-chondrites, could also deliver abundant water, but they would deliver other volatiles abundantly as well, in proportions very different from those on

Earth, as discussed below. At present, accretion of a few % C-chondritic material from the asteroid belt must be considered the leading hypothesis for the origin of most of Earth's water, as it would provide water in excess, at a time after nebular gas had dissipated and much Fe and H had already been sequestered into the core, so that most H delivered to Earth's surface would remain in its oxidized form as H₂O. Note that we are not referring to the so-called "late veneer", as this would have been added much later, after the core had fully formed, but rather to that part of Earth's main accretionary stage that took place after dissipation of the Solar nebula. Also note that no more than the necessary few percent carbonaceous chondritic material can have accreted to Earth, because its O isotopic content is so different from Earth's (Drake and Righter, 2002).

4.2. Loss of Earth's early atmosphere

There is no doubt that Earth suffered at least one and probably several episodes of massive atmospheric loss early in its history. Earth's present component of volatiles is therefore the small remnant of what was once present. The early atmosphere could have been eroded by intense UV radiation and winds during the million-year-long T-Tauri phase of the young Sun as well as by large impacts. UV radiation and winds would effect the lighter H atom most, but as the likely major constituent of an early Solar nebular atmosphere, produced in additional quantities by radiative splitting of H₂O (Zahnle, 2006), H streaming into space would pull heavier atoms such as Ne and molecules such as N₂ with it, in the thermally induced process known as hydrodynamic escape. Like the more gradual Jeans escape, it would mass-fractionate both elements and their isotopes, whereas mechanically induced atmospheric blowoff by giant impacts would fractionate to a much lesser extent if at all.

We have already noted the large depletion of the light isotopes ²¹Ne and especially ²⁰Ne relative to ²²Ne in Earth's atmosphere, compared with Solar Ne and mantle Ne. Isotopes of Ar show a similar pattern. Nearly all of the major Ar isotope on Earth, ⁴⁰Ar, has been produced by radioactive decay of ⁴⁰K. From the amount of K in Earth it can be inferred that about half of the ⁴⁰Ar produced is in the atmosphere (Palme and O'Neill, 2005); apparently the other half of the mantle has not degassed since the ⁴⁰Ar was produced within it (Morgan, 1998). The ⁴⁰Ar/³⁶Ar ratio in air is 296, but mantle ratios are much heavier: ~12,000 in the OIB source and ~30,000 in the MORB source (and ~40,000 in the crust), compared with an initial Solar ratio of 0.001–0.0001. Like Ne, mantle Ar is very different from atmospheric Ar. All mantle samples measured to date, however, are sufficiently contaminated with air such that

the ratio of their much less abundant primordial isotopes, ³⁸Ar/³⁶Ar, is indistinguishable from that of air at 0.188. (This is true as well for all six Kr isotopes.) This value is nearly identical to that of C-chondrites at 0.189, but much higher than the Solar wind value of 0.173. Thus, Ar in air, like Ne, is either meteoritic in origin or Solar but highly fractionated, with preferential loss of the light isotope ³⁶Ar. The latter explanation is far more likely.

More definitive evidence is provided by (1) the ²⁰Ne/³⁶Ar ratio, which is 30 in the Sun but only ~0.3 in the atmospheres of Earth, Mars, and Venus; and (2) the N/Ne ratio, which is 86,000 in Earth's atmosphere and one in the Sun (Zahnle, 2006). Clearly Earth's atmosphere has suffered >99% loss of the lightest Ne isotope. The apparent preferential loss of Ne (mass 20) to N₂ (mass 28) is so large that it probably also reflects addition of N to Earth as a condensate, rather than by capture from the Solar nebula or implantation by the Solar wind onto planetesimals (Owen et al., 2001).

Details about loss of the early atmosphere are provided by the nine Xe isotopes. Earth's atmosphere is generally depleted relative to the Solar pattern by ~4.2% per amu, indicating preferential loss of the lighter isotopes (Pepin and Porcelli, 2002). Recent high-resolution analyses of MORB and continental well gases have revealed for the first time a clear Solar pattern in the mantle for the three lightest isotopes (124, 126, and 128) (Pepin and Porcelli, 2006). Both of these observations reinforce the conclusions for Ne and Ar. What Xe offers in addition is that, besides their primordial component, ¹²⁹Xe and the heavier isotopes (131, 132, 134, and 136) were produced early in Earth's history by radioactive decay of, respectively, ¹²⁹I (half-life 15.7 Myr), ²⁴⁴Pu (half-life 82 Myr, and ²³⁸U (half-life 4450 Myr). The radioactive isotopes of I and Pu became extinct in our Solar System long ago, so the presence of their Xe daughter products in the atmosphere and in various mantle reservoirs records processes that occurred during Earth's first few hundred million years. Because there are three parent elements/isotopes with different half-lives, the absolute timing of atmospheric degassing and loss events can be estimated, and their relative timing even more accurately.

Pepin and Porcelli (2006) found that the key ratio of the radiogenic daughter isotopes in the two decay systems (¹²⁹Xe_{rad}/¹³⁶Xe₂₄₄) is similar in air and in the MORB source but greatly different in the well gases, thus identifying two distinct mantle reservoirs (although these two reservoirs have similar Ne isotopic ratios, according to Ballentine et al. (2005), who referred to them as "convecting mantle", as noted above). Yokochi and Marty (2005) identified a third distinct reservoir in the Kola carbonatite complex, representing the OIB/plume source, already distinguished from the MORB source by the isotopes of He, Ne, and Ar. Assuming that

iodine has not been heavily fractionated (an assumption that is likely but not yet certain), [Pepin and Porcelli \(2006\)](#) showed that the difference in $^{129}\text{Xe}_{\text{rad}}/^{136}\text{Xe}_{244}$ between MORB and the well gases requires two degassing events separated by 50–75 Myr. The sub-continental “convecting mantle” reservoir tapped by the well gases suffered massive Xe loss at 35 ± 13 Myr, followed by a similar degassing event for the MORB (shallow mantle) source and the atmosphere at 95–100 Myr. The former event likely tapped the mantle to greater depth ([Boyet and Carlson, 2005](#)) and may well be the Moon-forming impact that largely completed accretion of the Earth. The latter event may have been the first of several smaller impacts that were still large enough to degas part of the mantle and blow off much of Earth’s atmosphere: [Yokochi and Marty \(2005\)](#) showed that isotopic systematics of the Kola plume source require extensive loss of Xe not only during Earth’s first 100 Myr, but for several hundred Myr thereafter. Today, only 0.8% of the radiogenic ^{129}Xe produced over Earth history is still present in the atmosphere ([Pepin and Porcelli, 2002](#)).

4.3. Meteorites vs. comets as a source for Earth’s water

Although both probably contributed, meteorites are a much more likely source of the bulk of Earth’s volatiles than comets for several reasons, both chemical and dynamical. The D/H ratio of chondritic meteorites ([Robert, 2003, 2006](#)) is nearly identical to that of Earth at $\sim 150 \times 10^{-6}$ ([Table 1](#)), whereas in the only three comets measured it is twice as high at $\sim 310 \times 10^{-6}$ ([Eberhardt et al., 1995](#); [Bockelee-Morvan et al., 1998](#); [Meier et al., 1998](#)) ([Table 1](#)). The measured comets all originated in the Oort cloud, however, and rare comets originating in the Jupiter–Saturn region may have D/H ratios more similar to that of Earth ([Delsemme, 1999a, b](#)).

The overall pattern of depletion relative to the Sun of the eight highly volatile elements is remarkably similar in Earth and the C-chondrites ([Dauphas and Marty, 2002](#)), where the order, from most depleted to least, is He, Ne, Ar, Kr, Xe~H, N, and C. The only difference (a big one) is that on Earth, Xe is more depleted than Kr (and H): the “missing Xe” problem. [Dauphas and Marty \(2002\)](#) suggested that comets have a different pattern, based on experiments trapping gases in ice at low temperatures ([Owen and Bar-Nun, 1995, 2000](#); [Notesco et al., 2003](#); [Bar-Nun and Laufer, 2003](#)). The order of depletion in comets relative to the Sun would be He, H, Ar(?), Ne, Xe, Kr~N, C. Note that comets, like Earth, are more depleted in Xe than Kr, and so probably contributed to Earth’s volatiles ([Owen and Bar-Nun, 2000](#); [Dauphas, 2003](#)). However, the content

of noble gases in comets is inferred to be so much higher relative to H that if they were to deliver most of Earth’s water the excesses of noble gases would be measured in orders of magnitude ([Swindle and Kring, 1997](#); [Owen and Bar-Nun, 2000](#); [Drake and Righter, 2002](#)) (unless, again, the comets formed in the Jupiter–Saturn region). Whether this difference can be accommodated by the large losses of atmosphere discussed above is not clear.

Much has been written about the possibility of a “late veneer” delivering volatiles to Earth, along with the so-called “excess siderophile elements”. We have not discussed this issue because we concur with [Dauphas et al. \(2000\)](#) and [Drake and Righter \(2002\)](#) that most of Earth’s water was already present by the time any late veneer was delivered. [Levison et al. \(2001\)](#) furthermore showed on dynamical grounds that it is nearly impossible to deliver an ocean of water to Earth after the Moon-forming impact. In any case the isotopic composition of Os in Earth’s mantle precludes C-chondrites as the source of siderophile elements in a late veneer; rather the much drier ordinary (H-) chondrites are indicated ([Drake and Righter, 2002](#)).

4.4. Implications for astrobiology

There is much we do not yet understand about the origin and early history of water on Earth. What is clear is that water and other volatiles came from multiple sources by a variety of processes that were an integral part of formation of the Sun and the other planets. Because of our imperfect understanding and the complexity of the process, it is difficult to apply the insights from our own planet to other stellar systems. Nonetheless, it is encouraging that substantial water can be acquired by Earth-like rocky planets from a variety of sources, including the stellar nebula, the planetesimals that accrete to form the planet itself, and the wetter asteroids and comets that are likely to occupy most protostellar disks and to be added late in the accretionary process. With multiple opportunities to acquire water, wet planets like Earth are more likely to be common. It is encouraging as well that, in the case of Earth, an ocean of water and an atmosphere survived a truly catastrophic event such as the giant impact that formed the Moon, late during accretion and almost certainly after the oceans and atmosphere were present. Conditions for formation and survival of a habitable planet were clearly harsh at 1 AU in our Solar System, yet here we are: life originated and has thrived on our planet.

5. Water and microbial life

There is a commonality in the study of water’s properties as a solvent that extends across the fields of

astronomy, chemistry, geology, biology, and their intersection in astrobiology. We present here a brief overview of some of the basic relationships between water and astrobiology. (See also Chyba and Hand, 2005.) Because there is little argument that the earliest life on Earth was unicellular, microscopic, and anaerobic, we focus on the relationship between water and that which was Earth's first life, remains Earth's dominant form of life today, and is most likely to inhabit other worlds: microbes.

5.1. Water as a life support system

Water is an unusual liquid as a consequence of its dipolar molecular character (Fig. 3a). Water has a high boiling point, high heat of vaporization, and ice has a high melting point. Because the maximum density of water is at 4 °C it expands upon freezing, a most unusual behavior for a liquid-to-solid-phase transition. For biochemical reactions that depend on making and breaking of ionic and H bonds, one of the most important properties of water is its polarity, which makes it an excellent solvent for salts and polar molecules (Fig. 3b).

5.1.1. Polarity as a key property of water

It is difficult to imagine biochemical machinery that does not require water. The polarity of the water molecule (Fig. 3) enables many of its unusual properties, and ultimately dictates that the triple point of water, the point at which all three phases (solid, liquid, and gas) coexist, is within a range of temperatures close to the average temperature on Earth. Thus, water on Earth allows for a wide variety of climatic conditions, habitats,

and complex synergies between chemical and physical reactions (Schulze-Makuch and Irwin, 2004). The dipolar character of water makes it an ideal solvent for dissolution of a variety of salts required for metabolic reactions, and allows for hydrophobic organic molecules like lipids to make up cellular membranes. The persistence of hydrogen bonding in liquid water is key to understanding the physical properties of water, as well as its poorer solvent properties for non-polar, hydrophobic solutes.

5.1.2. Chemistry of solutes

Fig. 3b depicts a hydrated sodium ion, representative of ion–dipole bonds between ions and water. Dissolution of NaCl in water leads to a hydrated sodium ion surrounded by six water molecules in octahedral positions. Farther away from the central cation, additional water molecules are structured through dipole–dipole interactions. In a similar way, $\text{Cl}^-(\text{aq})$ ions also interact with the solvent water to form ion–dipole bonds, whereby orientation of the hydrogen side of H_2O points toward the central anion.

The dissolution of polar molecules in water is likewise favored by dipole–dipole interactions, while non-polar molecules are less favored for dissolution because of the unfavorable energy requirements for breaking and reforming hydrogen-bonded water. Ion–dipole, dipole–dipole, and H-bonding all contribute stabilizing and destabilizing properties to water, regardless of the complexity of the molecules or ions, and therefore lay the foundation for chemical speciation. Species of an element are distinguishable from one another stoichiometrically, structurally, and energetically, and the

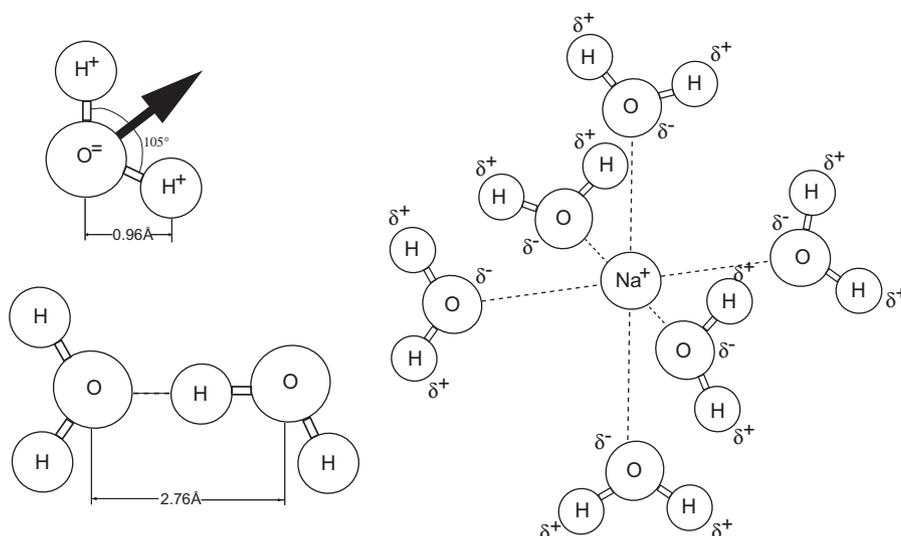


Fig. 3. (a) The structure of the angular water molecule and the hydrogen bond, illustrating the direction of the dipole moment, which gives water its distinctive properties in the liquid state (Horne, 1969); (b) hydrated sodium ion, Na^+ , in aqueous solution. H_2O molecules form ion–dipole bonds to the central metal ion. The waters are in octahedral coordination to the sodium ion (Gray, 1973).

Table 4. Summarized assessment of solvent candidates for selected planetary environments (from Schulze-Makuch and Irwin 2004)

Solvent	Earth	Icy satellite	Gas giant	Io (near subsurface)	Titan surface	Titan subsurface
H ₂ O	+4	+3	+1	+1	+1	0
NH ₃	−1	+1	+2	0	0	+3
HCN	+1	−1	0	−1	0	0
HF	−2	−1	0	−2	−3	0
H ₂ S	−4	−3	−3	0	−4	−2
CH ₃ OH	+1	+1	0	0	+1	+2
CH ₃ OH ₃	−4	−2	−3	−3	0	0

The metric is obtained by assigning +1 to four favorable characteristics (cosmic abundance, local abundance, enthalpy of vaporization, and dipole moment); by assigning −1 to unfavorable instances of the same characteristics; and by assigning 0 to cases that fall between favorable and unfavorable. Although largely speculative and crude, this estimate suggests that water is the best solvent on warmer bodies, while methanol may be superior in colder environments.

notion of chemical speciation is central to equilibrium and kinetic aspects of aquatic chemistry. Aquatic chemical speciation is of paramount importance for aquatic life.

5.1.3. Alternate possibilities to water as a life solvent

Oxygen is the most abundant element on Earth, and hydrogen is the most abundant element in the Universe, making it reasonable to assume that water should be commonly available as a solvent for life (Schulze-Makuch and Irwin, 2004). However, many of the environmental conditions that persist on Earth are relatively unique to Earth, and researchers have considered the notion that alternate solvents may play a role as a life-supporting system elsewhere. For instance, liquid ammonia has long been demonstrated to support construction of biomolecules (Chyba and Hand, 2005). Ammonia, however, and other polar solvents besides water, are only stable liquids at one atmosphere pressure at much colder temperatures. Consequently, biochemistry based on liquid ammonia at atmospheric pressures would proceed far more slowly than terrestrial biochemistry because of the exponential dependence of reaction rates with temperature (Chyba and Hand, 2005). However, biological catalysis of reactions substantially increases reaction rates, and at extremely high pressures ammonia could remain in liquid state up to its critical temperature of 132 °C (Schulze-Makuch and Irwin, 2004).

Schulze-Makuch and Irwin (2004) provide a concise quantitative assessment of candidates for life-supporting solvents (Table 4). They conclude that (1) water is the best solvent for Earth; (2) water is also the best solvent, perhaps in combination with ammonia and ethanol, beneath the surface of the icy satellites; (3) the gas giant planets do not favor any particular solvent except possibly water and ammonia within a particular thermal and pressure range; (4) the special circumstances of Io make it difficult for any solvent to function there, though some combination of water and H₂S might work

beneath the surface; (5) Titan's surface is inhospitable for any other than organic solvents; while (6) the subsurface of Titan could function with a combination of organic solvents, ammonia, and water. While alternate solvents for life are possible, much evidence is in support of the concept that water is a requirement for life. Furthermore, all known functional enzymes seem to retain 'internal' water bound strongly inside their protein structure, even if hydration-shell water primarily serves to promote flexibility and could be replaced by other solvents (Ball, 2004). Accordingly, this review focuses on water's relationship with known life processes on Earth and implications for possible life elsewhere.

5.2. Emergence of life

The debate about when and how life originated is an old one that continues today (Line, 2002; Trevors and Abel, 2004; Jortner, 2006). There is no evidence for life on Earth before the end of the late heavy bombardment at 3.85 Ga, but no sediments that are older survive, either. Favorable conditions may well have existed earlier and life may have begun, possibly even more than once, given that the Hadean aeon was characterized by frequent (every few 10⁶–10⁷ years) large meteorite impacts that would have heated surface environments to uninhabitable conditions (Nisbet and Fowler, 2003). The Archean aeon (4.0–2.5 Ga) was more stable and apparently was extremely favorable for the development and diversification of life (Martin et al., 2006).

5.2.1. Prebiotic chemistry

Environmental conditions and the chemical reactions that lead to emergence of life on Earth has been the subject of much speculation. It is not possible at present to date or even to identify the sequence of events that first produced living cells (Pascal et al., 2006). Yet some

active pre-biotic chemistry with an appropriate combination of characteristics led to chemicals with the capacity for storing, expressing, and transmitting genetic information, which were then subjected to forces of natural selection. Pascal et al. (2006) and Jortner (2006) review some of the conditions necessary for the emergence of life on Earth, including availability of (1) liquid water; (2) biotic raw materials including elements (C, H, N, O, P, S, Fe, Mg, etc.), simple molecules (H_2 , H_2O , NH_3 , CO , CO_2 , H_2S , CH_4 , etc.), and minerals containing Si, Fe, Ni, P, and S; (3) clay minerals or other suitable substrate; and (4) chemical and thermal conditions that permit energy acquisition and disposal by functional biology, such as the conversion of light energy into chemical energy and/or the use of chemical energy through donor-acceptor electron transfer.

5.2.2. The first life on Earth

All organisms present on Earth today (not including viruses) are based upon a hierarchy of cellular organization, consisting of five major functions: metabolism, growth (reproduction), differentiation, chemical communication, and evolution (Pascal et al., 2006). The first organisms were therefore also probably organized on a cellular basis. While fossil evidence suggests that photosynthesis arose early, the oxygen produced was consumed by mineral oxidation and only reached roughly 10^{-5} of today's atmospheric concentration by 2.32 Ga (Bekker et al., 2004), signifying that the first organisms on Earth developed under anoxic conditions (Nealson and Rye, 2003; Schulze-Makuch and Irwin, 2004; Canfield et al., 2006). We proceed with the safe assumption that life must be capable of using available free energy to maintain disequilibrium from its environment.

5.2.3. Emergent metabolisms

Biology distinguishes itself by its capability to sustain and extend its environmental conditions. We know of only two ultimate sources of energy for life on Earth: light from the Sun and geothermal (chemical) energy. The mechanism whereby life harnesses useful energy from the environment appears to be nearly universal, involving the use of redox energy to pump ions (typically protons) across an impermeable membrane, thus setting up a charge separation that can subsequently be exploited to drive the synthesis of adenosine triphosphate (ATP), the base unit of energy for living systems. This fundamental metabolic process of life can be quantified by the gap of the redox separation, with larger charge separation yielding higher energy, and pumping more ions, ultimately allowing for more ATP production (Nealson and Rye, 2003). While photoautotrophs can directly capture and utilize light energy, other organisms utilize reduced organic or inorganic molecules, many of which are generated as a result of

geothermal processes. Energetically favorable redox reactions are the foundation for life on Earth under today's oxic conditions. Anaerobic metabolisms that persist in anoxic environments allow us to infer possible early-Earth metabolisms.

Whatever metabolism(s) is(are) favored by an ecosystem, there is a principle difference between availability of compounds used for synthesizing biomass and those required for energy conservation. While nutrient limitation induces a decrease in metabolic activity, the lack of an energy substrate forces an organism to relocate or switch to a different type of metabolism. It may even cause a shift in the composition of a microbial community (Brune et al., 2000). Through such mechanisms both microbes and higher organisms create local order by using Sunlight and/or geothermal energy to exploit and create redox contrast between the surface of Earth and its interior (Nisbet and Fowler, 2003). This pattern persists today, as in a typical profile in marine sediments or stratified water bodies (Fig. 4), and has probably prevailed throughout Earth's history, as Earth was transformed from an exclusively anoxic to a largely oxic environment.

5.2.4. A universal context

Although there is no direct evidence that life exists elsewhere in the Universe, there are characteristics of some environments both on Earth and elsewhere that suggests the capability for supporting life is probably not limited to our home planet. Discoveries of extremophilic microbes have expanded the range of physical and chemical conditions possible for supporting terrestrial life and have made many researchers less skeptical regarding the possibility for similar biology elsewhere in the Universe (Montmerle et al., 2006b; Chyba, 1997; Sagan, 1996). Recent discoveries, including evidence that water once flowed on Mars (Squyres and Knoll, 2005), the presence of liquid oceans on the Jovian moons Europa, Callisto, and Ganymede (Lipps and Rieboldt, 2005; Scott et al., 2002), and organic molecules on the Saturnian moon Titan (Mitchell, 2007), have fueled exobiological interest within and beyond our Solar system (Dick, 2006). We now follow life in Earth's challenging environments and its implications for extraterrestrial environments.

5.3. Challenging aqueous habitats for life

On Earth, life has adapted to cope with the varied conditions of the environment. Specialized protein biochemistry, niche selection, and metabolic diversity all can aid microbes in dealing with "extreme" environments. Microbes have been found throughout Earth's diverse biosphere, from 77 km high in the atmosphere to hundreds of meters below the seafloor (Cowen et al.,

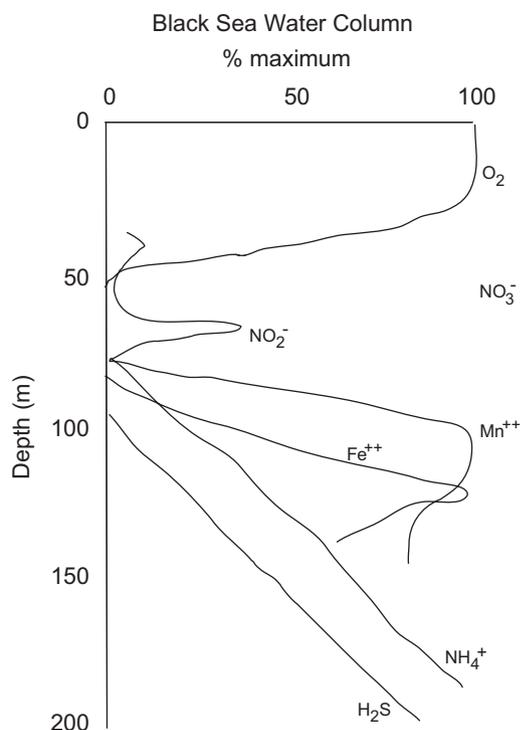


Fig. 4. Energetics of redox reactions lead to typical biogeochemical stratification in aqueous systems following well-established thermodynamic predictions (adapted from Nealson et al., 1997). For example, oxidation of organic matter by oxygen is a very favorable reaction, and after oxygen is depleted, a series of electron acceptors diminishing in redox potentials are consumed (NO_3^- , MnO_2 , FeOOH , SO_4^{2-} , etc.).

2003), from the interior of Antarctic ice cores (Abyzov, 1993) to surfaces near submarine 350°C hydrothermal vents (Deming and Baross, 1993). Habitats on Earth vary from largely uniform over a large area or volume (deserts, oceans) to extremely vary over small scales (coral reefs). Biological diversity generally increases with increased heterogeneity due to the presence of more niches to which different forms of life can become optimally adapted (Schulze-Makuch and Irwin, 2004).

Nearly all sites on and in Earth where an energy source is available appear to be inhabited by microbial communities (Horneck, 2000). All extant organisms are based in a cellular matrix, using the same basic set of amino acids and similar lipid membranes to separate themselves from their environment. Of the behavioral, ecological, or physiological adaptations that organisms have evolved to cope with harsh environmental niches, probably the most useful is that of biochemical metabolic diversity. Once life was established on Earth it has been very resilient. Life has persisted and occupied every explored niche on this planet, including several that are especially challenging. Here, we summarize four such aqueous habitats that present unique challenges for life.

5.3.1. Dry environments

Some microbes have developed mechanisms to grow and/or survive at much lower water activities than required by most organisms. Some strategies provide shelter, as is the case with cryptoendolithic microbial communities found in hot and cold deserts. Such microbes colonize sandstones a few millimeters below the surface, forming layers of algae and cyanobacteria as primary producers and fungi and bacteria as consumers (Horneck, 2000). Alternatively, some organisms have developed a tolerance to desiccation by developing good reserves of high-energy compounds, membrane stabilizers, or spore-forming stages (Horneck, 2000; Kuhlman, et al., 2005; Thiagarajan and Aeolus Lee, 2004).

With its current thin atmosphere, the surface of Mars provides an extremely cold and dry climate, often compared with the Dry Valleys of Antarctica as an analog environment. If life once existed on the surface of Mars, it is likely that it retreated into the Martian subsurface (Rothschild, 1990). If so, cryptoendolithic communities on Earth may be suitable models for adaptation to the suite of extreme environmental stresses (including low water availability, ultraviolet intensity, oxidizing chemistry, etc.) on the Martian surface during the cooling phase of its atmosphere (Horneck, 2000).

5.3.2. Brines and evaporites

When natural waters evaporate the dissolved minerals become more concentrated, forming a brine and then progressing to precipitation of evaporite deposits (Mancinelli et al., 2004). Brines and evaporites characterize a highly saline habitat that is hostile to most organisms, but ideal for halophiles. Hot and cold hypersaline lakes, Solar salterns, deep-sea brines, and hypersaline soils are halophilic environments found on Earth that probably had analogs on Mars at some time during its history (Mancinelli, 2005). Halophilic microorganisms live in hypersaline environments ranging from 15 wt% to saturation for salt content (Mancinelli, 2005). At such concentrations of salt, organisms must be specially adapted to withstand osmotic pressure, as non-halophiles generally cannot tolerate osmotic stress. Many halophiles respond to increases in osmolarity by accumulating organic osmotic solutes within their cytosol (Mancinelli, et al., 2004), providing protection from dehydration and desiccation. Recent studies have produced models for stromatolite formation in open marine systems and lithification in shallow hypersaline lakes that are highly relevant for interpreting the rock record and searching for extraterrestrial life (Dupraz and Visscher, 2005).

5.3.3. Ice

Psychrophiles are organisms that preferentially subsist in colder environments. On Earth, psychrophilic

microbes are found in permafrost (Rivkina et al., 2004), ice sheets (Vincent et al., 2004), and subglacial lakes (Abyzov et al., 2001). Microbial cells have been detected in glacier ice cores at depths of 3.6 km, corresponding to an interfacial zone between basal and accretionary ice at the surface of subglacial Lake Vostok, Antarctica (Abyzov et al., 2001). Lake Vostok has held considerable interest for a number of years because of its potential for containing relict forms of life on Earth (it has been sealed from the rest of Earth for a million years or more) and as an analogue for ice-covered oceans on the Jovian satellites Europa, Ganymede and Callisto. Numbers of cells from ice horizons just above the subglacial lake range from hundreds per milliliters (Karl et al., 1999) to nearly an order of magnitude higher (Priscu et al., 1999), suggesting that the upper layers of accreted ice from Lake Vostok contain microorganisms from upper ice sheet horizons, moraine material, and lake water (Abyzov et al., 2001). It is unclear how metabolically active most psychrophiles are at extremely low temperatures, but recent evidence suggests growth at temperatures as low as -20°C , with slow doubling times of ~ 180 days. For mere survival without growth, cold temperatures provide little barrier to microbes, as freezing in liquid N_2 is a common technique for preservation of cells, and dry bacterial spores have been shown to survive temperatures down to -263°C .

5.3.4. Hydrothermal systems

The discovery of deep-sea hydrothermal vents including 350°C “black smokers” opened new research fields into extremophilic chemosynthetic life (Priour, 2005). Vent fluids are chemically distinct from seawater, generally characterized by low pH and high concentrations of reduced inorganic compounds and dissolved gases resulting from seafloor hydrothermal circulation and rock–water interactions. It has been proposed that the chemoautotrophic origin of life evolved in a volcanic iron–sulfur-rich environment similar to that of hydrothermal vents (Wächtershauser, 2006). Indeed, the vents provide for a variety of electron donors and acceptors that are utilized by thermophiles and/or hyperthermophiles.

Of considerable interest is the growing evidence for a large seafloor biosphere (Whitman et al., 1998; Cowen et al., 2003; Edwards et al., 2005; Neelson et al., 2005). Life may have originated in the subsurface, protected from catastrophic events such as volcanic eruptions and meteorite impacts (Trevors, 2002). While the biomass in the seafloor may be large, metabolic rates measured to date are low (D’hondt, et al., 2002), indicating that most prokaryotes are inactive or metabolically slow (Parkes, et al., 2005). The issue of growth rates and metabolic efficiencies of seafloor microbes will be important to resolve within the context

of planetary evolution because it is not clear that rapid growth is a prerequisite for ecosystems in the early Earth (Neelson et al., 2005).

5.4. Other planets as habitats

Recent technological advances have provided insight into the present and past conditions of many of Earth’s neighbors. Venus may have had the right proximity to the Sun at one time to host water oceans and life (Kasting et al., 1993), but has since lost all of its hydrogen (i.e., water; Donahue et al., 1982; Watson et al., 1984). Tectonic activity on Mars has ceased and the planet has lost the ability to renew its surface, losing most of its CO_2 atmosphere and turning into a freeze-dried desert (Chyba and Hand, 2005). The discovery of the subsurface biosphere on Earth has impacted our thinking about prospects for life elsewhere (Sagan, 1996; Chyba, 1997). It is even imaginable for planets that have been ejected from their parent star and are floating free in space to remain habitable for subsurface life, provided sufficient geothermal activity permits liquid water at depth. Additionally, Lunar and Martian meteorites have shown that surface material can be exchanged between planets (Taylor, 2001).

As of September, 2007, 212 extraSolar planets have been discovered (Exoplanets.org, 2007), and technologies are developing to give supporting evidence for the presence of water on some (e.g., Tinetti et al., 2007). A key goal of the proposed Terrestrial Planet Finder and Darwin space missions is the spectroscopic detection of water on terrestrial planets orbiting other stars. As mentioned above, while solvents other than water may be sufficient for hosting complex biochemical reactions, much more work is needed to demonstrate the feasibility of possible chemical mechanisms. Even if solvents other than water prove to be incapable of supporting life, and life is restricted to water-abundant bodies such as Earth and possibly Mars and Europa (Schulze-Makuch and Irwin, 2004), the sheer number of planets and moons that surely exist in the Universe, combined with the abundance of oxygen and hydrogen, make widespread life as we know it a distinct possibility. Schulze-Makuch and Irwin (2004) summarize the likelihood for various bodies in our Solar System to support life using a Plausibility of Life – POL – rating, pseudo-quantifiable on a scale of I–V based on abundance of water, organics, and an energy source. Earth, gratifyingly, gets a POL rating of I, while the Moon is rated only V because it is too dry, lacks an atmosphere, and lacks geological cycling. Venus, Mars, Europa, Ganymede, and Titan are rated II. While the possibility exists for other bodies, including comets and asteroids, to support life, we focus below on Mars, Europa, and Titan.

5.4.1. Mars

Although Mars is now largely inactive geologically, massive volcanism and possibly even plate tectonics occurred at some time in its past (Acuna et al., 1999). Such activity could have provided an energy source to support life (Jakosky and Shock, 1998). Aside from possible parallel origins for life, it has been proposed that “lithopanspermia” could have occurred between Earth and Mars, especially during the period of heavy bombardment prior to 3.8 Ga (Wells et al., 2003; Stetter, 2006; Stoffler et al., 2007). In any case, it is likely that similar habitable niches existed on both early Earth and early Mars. At its smaller size Mars would have cooled much faster than Earth. If its surface cooled earlier life could have begun on Mars before it did on Earth, if life originated in shallow water habitats (Westall, 2005). Martian life would then have progressed to evaporitic and halophilic habitats with increasingly arid conditions, ultimately resembling the Antarctic Dry Valleys of Earth today, where cryptoendolithic microbes are found.

The discoveries by the two Mars Exploration Rovers have greatly expanded our understanding of the history and current status of liquid water on Mars (Squyres et al., 2004). In particular, the presence of sulfate salt deposits in the Meridiani Planum strongly suggests that the region has been inundated by large volumes of liquid water. Comparisons have been made between outcrop rocks at Meridiani Planum and the mineralogy and sedimentary geobiology of the Rio Tinto Basin, Spain (Fernandez-Remolar et al., 2005), as biologically mediated oxidation of pyritic ore bodies in the source area of the Rio Tinto generates headwaters enriched in sulfuric acid and ferric iron. Gaining a better understanding of biosignatures that may be imparted to sedimentary rocks during iron oxidation in areas like Rio Tinto should help to elucidate the history of water and any biological oxidation activity on Mars (see also Tokano, 2005).

5.4.2. Europa

Europa is an ice-covered moon of Jupiter, roughly the same size as Earth’s Moon. It is among the most interesting targets in our Solar System for astrobiology because it probably hosts a deep ocean of liquid water beneath an icy shell 10–30 km thick (Carr et al., 1998). Gravity measurements from the Galileo spacecraft to showed that Europa is an internally differentiated rocky body with a surface layer 80–170 km thick of density 1000 kg/m. Europa is locked in mean-motion (or orbital) resonance with Io and Ganymede, two other satellites of Jupiter, which likely would lead to enough tidal flexing and internal energy dissipation to maintain most of the ice layer as liquid water. Possible sources for supplying an environmental chemical disequilibrium on Europa include charged-particle radiation (Chyba and

Phillips, 2001; Chyba and Hand, 2005) or possible hydrothermal activity (McCullom, 1999), though biomass that could be supported would be low (see also Lipps and Rieboldt, 2005).

5.4.3. Titan

Titan is Saturn’s largest moon and represents an intriguing natural laboratory due its cold temperatures (~94 K), lack of liquid water, and apparently complex carbon cycle involving methane clouds, photolytically derived hydrocarbons, and erosion-riddled surface (Chyba and Hand, 2005). Titan is a complex world, apparently impacted by tectonic, atmospheric, and fluvial processes similar to those on Earth; however, rates of such physical activities on Titan are likely to be much slower (Porco et al., 2005). The 2005 cooperative NASA-ESA Cassini/Huygens mission (Lebreton et al., 2005) and resulting data has kept the spotlight on Titan as a prominent target of astrobiological importance. Particularly interesting are the direct atmospheric measurements from the gas chromatograph–mass spectrometer that confirm the abundant presence of nitrogen and methane in Titan’s thick atmosphere (Niemann et al., 2005). These measurements have provided insight into the photochemistry that forms complex hydrocarbons and nitriles. Also of note is the likely detection of water ice (Porco et al., 2005), which has spawned new laboratory experiments simulating the chemical evolution of Titan’s surface. These experiments have generated C–H–O, C–H–N, and C–H–O–N compounds by electrical discharge (Plankensteiner et al., 2007). Titan has become a priority target for future studies, perhaps at the expense of Mars (see also Lorenz et al., 2005).

5.5. A note of caution

Although much consideration for possible habitability is given to the presence of liquid water, life as we know it demands as well a suite of biogenic elements (i.e., C, H, O, N, P, and S) and a usable form of free energy (Chyba and Hand, 2005). It is likely that an environment without volcanism, and therefore lacking an abiotic source of redox disequilibrium, would have little to offer life because of a lack of readily available free energy. While the presence of water is a key parameter in the search for astrobiology, the presence of chemical gradients, because of their potential for generating free energy, is equally important and should not be overlooked (Schulze-Makuch and Irwin, 2004).

6. Concluding remarks

Much remains to be learned about water in the Universe and its relationship with life. We are beginning

to learn how water behaves in interstellar space as both observational and laboratory experimental techniques improve. Because water is one of the most abundant materials in the Universe, water ice plays a key role as both a substrate and a reactant in space, aiding in formation of surprisingly complex organic molecules. Increases in computing power and chemical analytical techniques, especially mass spectrometry on small samples, have led to rapid advances, but we still do not have a clear understanding of the history of water in our Solar System and how it came to be distributed as it is. While it appears that Earth acquired its water by a variety of means, including (slightly) wet accretion, gravitational capture of nebular gas followed by dissolution into a magma ocean, and later accretion of wetter planetesimals from the asteroid belt as well as comets, it is clear that the processes of Earth formation were accompanied by massive loss of the atmosphere on more than one occasion. Accordingly, we still do not have a satisfactory theory for the origin of Earth's oceans and atmosphere, nor do we know the relative importance of the various processes by which water came to Earth and was retained. Nonetheless, it is promising for the prospect of extraterrestrial life that small rocky planets in a star's habitable zone can apparently acquire and retain water through a variety of means during formation of a planetary system.

There is nothing that is obviously unique about the way Earth formed and became a cradle for life, although the timing and result of the Moon-forming giant impact (a rapidly spinning Earth with a single large Moon that stabilizes Earth's axial tilt) may be unusual. The orbits of the giant planets in our Solar System are also favorable, being nearly circular and far enough away to create a stable habitable zone, allowing delivery of sufficient volatiles to Earth but limiting the long-term rate of bombardment by comets. While life as we do not know it may have originated and thrived elsewhere on compounds other than water, water still seems by far the best medium for life because of its unusual chemical and physical properties. On Earth, life is amazingly adaptive, having evolved multiple mechanisms to tolerate a wide range in temperature, salinity, acidity, and abundance or scarcity of water. Some scientists are optimistic, therefore, that at least microbial life will have found vital niches elsewhere in our Solar System. There is every reason to expect that Earth-like environments exist elsewhere in our galaxy, as well, and that we will eventually discover them, bringing the study of astrobiology to a new level.

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