ACADEMIC PRESS

The origin of water on Mars

Jonathan I. Lunine,[a,*] John Chambers,[b,c] Alessandro Morbidelli,[d] and Laurie A. Leshin[e]

[a] Lunar and Planetary Laboratory, The University of Arizona, Tucson, AZ 85721, USA
[b] SETI Institute, Mountain View, CA 94043, USA
[c] NASA Ames Research Center, Mountain View, CA 94035, USA
[d] Observatoire de la Côte d'Azur, BP 4229, F-06304 Nice cedex 4, France
[e] Department of Geological Sciences, Arizona State University, Tempe, AZ 85287, USA

Abstract

This paper considers the origin of water on Mars, in the context of a dynamical model that accounts for most of the Earth's water as a product of collisions between the growing Earth and planet-sized "embryos" from the asteroid belt. Mars' history is found to be different; to explain the present mass of Mars requires that it suffer essentially no giant collisions and the bulk of its growth is through addition of smaller bodies. Asteroids and comets from beyond 2.5 AU provide the source of Mars' water, which totals 6–27% of the Earth's present ocean (1 Earth ocean $\equiv 1.5 \times 10^{21}$ kg), equivalent to 600–2700-m depth on the martian surface. The D/H ratio of this material is 1.2–1.6 times Standard Mean Ocean Water, the smaller value obtaining for the larger amount of water accreted. The upper half of the range of total water accreted, while many times less than that acquired by the Earth, is consistent with geological data on Mars, and the D/H value is that derived for martian magmatic water from SNC meteorites. Both together are consistent with published interpretations of the high D/H in present-day martian atmospheric water in terms of water loss through atmospheric escape.
© 2003 Elsevier Inc. All rights reserved.

Keywords: Origin, Solar System; Mars, interior; Mars, atmosphere; Planetesimals

1. Introduction

In the search for habitable planets around other stars, astronomers will focus on the so-called continuously habitable zone (CHZ) in which sufficient insolation is available from the parent star to ensure liquid water over much of the star's main sequence lifetime. For stars like the Sun, this paradoxically puts the planet at an orbital distance that, according to typical protoplanetary disk models (Cassen, 1994), would have been quite hot for much of the time during which solids were formed. Indeed, in our own solar system, both models and meteorite data suggest that the one astronomical unit (1 AU) zone where the Earth formed was too hot for water to be directly incorporated in local planetesimals, implying that water was acquired by our own planet from material that formed at larger distances from the Sun (Robert, 2001).

Morbidelli et al. (2000) showed on dynamical and chemical grounds that the Earth could have acquired all of its crustal and surface waters from large "planetary embryos" which grew in the asteroid belt during terrestrial planet formation. The source is consistent with current understanding of the water content of the asteroid belt as informed by the chondritic meteorite record (Robert, 2001), and with the role of the giant planets in clearing the primordial asteroid belt (Petit et al., 2000). It is consistent with the isotopic record of D/H in ocean water and in carbonaceous chondrites. It is constrained but not contradicted by the trends of oxygen and other isotopes in Earth and chondritic meteorites, which limit the total amount and timing of delivery of water from the asteroid belt (Drake and Righter, 2002). Comets are ruled out on isotopic (Meier et al., 1998) and dynamical (Morbidelli et al., 2000) grounds as the primary source of Earth's water, contributing no more than 10% of the crustal and surficial water budget. A local source of water for the Earth would require low nebular temperatures for the formation of hydrated planetesimals at 1 AU (astronomical unit) during the era of solids formation, and seems to contradict the meteoritic evidence suggesting that material inward of 2.5–3 AU was too dry to supply an ocean or more of water.

* Corresponding author.
  E-mail address: jlunine@lpl.arizona.edu (J.I. Lunine).

A principal source of Earth's water in the asteroid belt must have implications for the total amount of water that Mars acquired during its formation. At first glance, one might imagine that Mars should have gained more water since it is closer to the asteroid belt that is the Earth. However, planetary growth is strongly stochastic (Chambers and Cassen, 2002), and therefore one cannot simply extrapolate the delivery of material to Mars from the case of the Earth. In this paper, we analyze the results of published dynamical simulations to argue that Mars probably acquired *less* water than did the Earth, about 0.06–0.27 of an Earth's ocean (1 Earth ocean $\equiv 1.5 \times 10^{21}$ kg, which includes crustal waters that exchange with the ocean). The original D/H value for martian water exceeded that of the Earth's oceans. We then compare these numbers to constraints on the early inventory of martian water, and the D/H value inferred from SNC meteorites. We show that the initial abundance and D/H value of water delivered to Mars are consistent with these constraints and with the current D/H value for the martian atmosphere corrected for the deuterium enrichment caused by atmospheric escape.

2. General description of the dynamical model

The techniques and assumptions used in the dynamical simulations have been described previously (Petit et al., 2000). For statistical purposes, we have analyzed eleven simulations where terrestrial planets are assumed to form from a population of Mercury-to-Mars-mass planetary embryos ranging in position from 0.5–4 AU. Two of the simulations were done using the symplectic Mercury integrator, written by J. Chambers, and nine of them, using a precursor code to Mercury that was not symplectic, were presented elsewhere (Chambers and Wetherill, 1998). More recent models (Chambers and Cassen, 2002) produce results that are, for the purposes of this study, consistent with the eleven cases we analyzed, with the caveat that accounting for the initially more eccentric orbits of the giant planets decreases the number of embryos accreted by the terrestrial planets from the asteroidal region. This should not affect our results for Mars, for the reasons described below, but may affect the amount of water the Earth acquired from embryos formed beyond 2.5 AU (Morbidelli et al., 2000).

The runaway process that led to the formation of planetary embryos spanned the realm of the terrestrial planets as well as the asteroid belt. Mercury-to-Mars-mass planetary embryos, separated by a few mutual Hill's radii, are presumed to have formed all over the inner solar system on quasi-circular and coplanar orbits. What is typically observed in the simulations is that mutual perturbations among the planetary embryos force their eccentricities to mildly increase, so that their orbits cross each other and the embryos start to have mutual close encounters and accretional collisions. The asteroids (of negligible mass with respect to the embryos, so that they behave as test particles, do not interact with each other and do not perturb the embryo's dynamics) are gravitationally scattered by encounters with the embryos and acquire orbits with large eccentricities and inclinations. Most of the asteroids, however, stay within the borders of the presently observed asteroid belt.

As Jupiter accretes its gaseous envelope and approaches its current mass, the dynamical evolution of the system changes abruptly, because the distant perturbations of the giant planet become effective, and powerful mean motion and secular resonances—capable of pumping the eccentricity to very large values—appear in the asteroid belt. Because of their semimajor axis mobility, induced by mutual encounters, the embryos in the asteroid belt temporarily fall into one of these resonances, thereby acquiring larger eccentricities. Therefore, the embryos initially in the asteroid belt have three possible fates. In order of decreasing likelihood, they are

(i) to intersect Jupiter's orbit and be ejected on hyperbolic orbits;
(ii) to cross the orbits of the growing terrestrial planets and be accreted by the latter on a longer timescale;
(iii) to have their eccentricities pumped to unity by some resonance with Jupiter and therefore collide with the Sun.

The same does not happen to the embryos with semimajor axes less that 2 AU because over planetary formation timescales they do not encounter Jupiter and are not ejected. Moreover, in the region of such embryos the resonant perturbations of Jupiter are much less effective than in the asteroid belt. Therefore, at the end of the simulation the asteroid belt is cleared of embryos, while within 2 AU of the Sun one to several planets with masses comparable to that of the Earth have been formed, depending on the particular run.

The formation of Mars in this picture remains, somewhat surprisingly, problematic. Simulations in a gas-free environment of the evolution of Mercury-to-Mars-mass embryos fail to leave a Mars-mass object in an orbit similar to that of present-day Mars; rather, much more massive planets are formed (Chambers and Cassen, 2002). Inclusion of gas, which damps the eccentricities of the embryos, leads to the formation of a number of very small planets (Kominami and Ida, 2002a). Time-dependent removal of the gas alters the results somewhat (Kominami and Ida, 2002b), but the configuration of our solar system, in which a Mars-mass body exists just beyond two roughly Earth-mass planets, remains elusive. We believe that this does not indicate a failure of the dynamical models to include the proper physics, but rather illustrates the stochastic nature of terrestrial planet formation and the large number of outcomes that are possible in reality. We therefore adopt the hypothesis that Mars is an embryo that escaped either ejection or accretion, and in what follows we pursue the implications of this hypothesis for the amount and sources of water that Mars acquired.

During accretion, three agents deliver water to the growing terrestrial planets:

(i) planetary embryos from beyond 2.5 AU,
(ii) small asteroids from beyond 2.5 AU, and
(iii) comets from the Jupiter region and beyond.

Assuming an Earth mass of asteroid material in the outer main belt, the small asteroids can bring to the Earth 20% of the current crustal and surficial water. Assuming 50 Earth masses of comets in the Jupiter–Saturn region and 50 Earth masses beyond Uranus, comets could have delivered some 10–15% of crustal and surficial water to the Earth. The principal delivery of material by comets occurred earlier than delivery of material by planetary embryos from the asteroid belt as comets were scattered quickly by growing Jupiter.

The total amount of water that could have been delivered by the embryos is roughly 5 to 10 times the amount of water in the crust and on the surface of the Earth today. However, oxygen and osmium isotopic evidence (Drake and Righter, 2002) limit the amount of carbonaceous chondritic material (our model for the water laden planetary embryos in the asteroid belt) accreted by the Earth to a few percent of our planet's total mass—provided this was accreted before core formation occurred (the limit is 1% for material added after core formation). A few percent is still enough to supply the crustal and surficial water observed on the Earth today, even if on average half the water is retained during the impacts between the embryos and the growing Earth. (Genda and Abe (Icarus, in press), present results that suggest that most of the accreted water is retained by an Earth-mass body if the impactor is roughly the mass of Mars or less; R. Canup and colleagues (in preparation) are quantifying the retention of water during giant impacts as a function of the mass of the growing Earth.)

3. Constraints from deuterium

The primary isotopic ratio with which we can constrain our model is the deuterium to hydrogen ratio (D/H). Figure 1 shows the D/H value for chondritic meteorites compared to comets and the Earth. SMOW or Standard Mean Ocean Water is well determined at a value of 156 parts per million deuterium-to-hydrogen by number (Robert et al., 2000). Carbonaceous chondrites contain two rather different carriers of hydrogen, namely the clay minerals and the organic compounds. The latter are systematically rich in deuterium, with D/H over twice SMOW. The clay minerals, which are most likely to represent the deuterium abundance in bound water, have a mean D/H close to SMOW, though in a small number of samples D/H is significantly enriched (Robert, 2001).

The carbonaceous chondrites are presumed, on the basis of both dynamical arguments and remote sensing studies of asteroids, to represent material from the 2.5 to 4 AU region of the solar system dating back to the formation
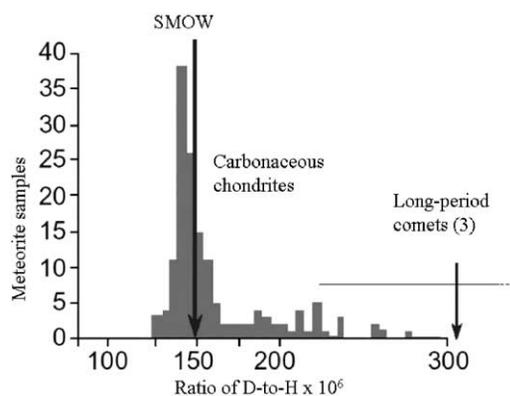

Fig. 1. Ratio of deuterium to hydrogen in various carbonaceous chondrites compared with the value for Earth (SMOW) and the value (with error bar) for three Oort Cloud comets. Redrawn from Robert (2001).

of the planets. However, there are variations in major elements abundances (e.g., Mg/Si vs. Al/Si) that suggest that multiple reservoirs of material with distinct composition resided in the asteroid belt (Drake and Righter, 2002). Based on measurements of D/H in carbonaceous chondrites, and their inferred relationship to parent bodies in the outer region of the asteroid belt, we assume that primordial material in the asteroid belt had D/H approximately SMOW (Robert et al., 2000). Measurements of D/H in water from three long-period (Oort-cloud) comets yield values twice SMOW (Balsiger et al., 1995; Bockelée-Morvan et al., 1998; Meier et al., 1998). Comets do not belong to a single class of primitive material, and the three comets in which D/H in ice has been measured are all Oort cloud comets, derived originally from the giant planet region (Meier et al., 1998). Short period comets derive from the Kuiper Belt (Levison and Duncan, 1994), and hence, if anything, should have *higher* D/H than do the Oort cloud comets, though not necessarily much higher because the kinetics are highly unfavorable for extensive enrichment of deuterium in ice at outer solar system temperatures. Thus, while our assumed values of D/H for various types of primitive bodies is simple, they are consistent with what we know about the source regions of these bodies, and more complicated compositional dependencies would be *ad hoc* given the scarce data available.

The value of D/H of water in the current martian atmosphere is 5.5 SMOW (Owen, 1992) and the cause of the elevation relative to the terrestrial value is commonly ascribed to isotopic fractionation during atmospheric escape of water that is exchanging with sources of water in the martian crust and surface (Donahue, 1995; Owen, 1992). However, the original value of D/H in martian water, that is, the value obtained from the planetesimals that brought water to the red planet, is not well known. Fractionation calculations tend to assume SMOW as the starting value, without any justification (Krasnopolsky, 2000). In fact, as described below, the evidence from martian (SNC) meteorites suggests that the initial D/H value for martian interior water was higher.

The D/H values of magmatic, hydrous minerals—apatite, Ti-rich amphibole, and biotite—have been analyzed in five martian meteorites by ion microprobe (Leshin, 2000; Rubin et al., 2000; Watson et al., 1994). The elevated and variable D/H values of water discovered in these primary, hydrated, minerals ($\delta D \sim +800$ to $+4300$) are interpreted qualitatively as representing a mixture of martian magmatic water in the minerals with a D-enriched component derived from the martian atmosphere (with the D/H value 5.5 SMOW), through isotopic exchange with deuterium-enriched groundwaters introduced after the phases crystallized from their host martian magmas. (δD notation expresses the deviation of a measured D/H ratio from that of SMOW in parts per thousand; the range of δD values on Earth (Hoefs, 1997) is about $+100$ to $-300‰$.) The presence of a "meteoric" (atmosphere-derived) D-rich component is also indicated by ion microprobe analyses of carbonates in ALH84001, which have D/H values up to twice SMOW (Sugiura and Hoshino, 2000).

Of specific value in constraining the isotopic composition of the magmatic (low D/H) end-member are data from apatite in martian meteorite QUE 94201, in which both D/H and water contents were analyzed (Leshin, 2000). In this case, the isotopic measurements show a correlation with the OH content of the apatite (Fig. 2). The data are suggestive of mixing between two isotopically distinct hydrogen reservoirs because most physical processes (e.g., degassing) are incapable of producing the $\sim 2000‰$ isotopic variation that is observed. Because mixing with atmosphere-derived, D-enriched waters (or any other reasonable process to change the D/H of these minerals) would tend to increase their D/H values, magmatic water must be the low-D/H end-member of the trend in Fig. 2. A best fit mixing model to account for the variation of the QUE 94201 apatite data gives a value
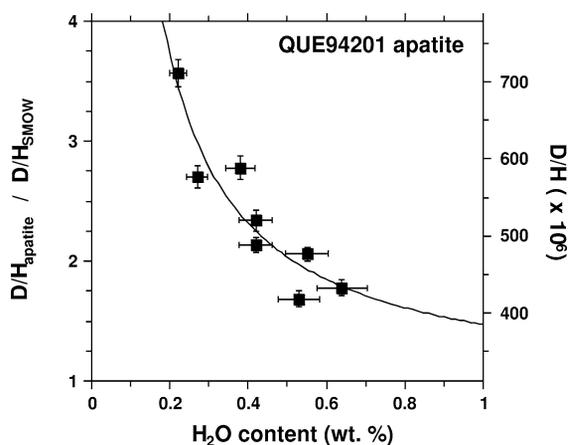

Fig. 2. D/H and water contents of apatite grains from martian meteorite QUE94201, after Leshin (2000). The data are interpreted to represent a mixture of two end members, and most plausibly represent addition (or exchange) of water with an atmospheric D/H signature (D/H $\sim$ 5 times SMOW) to minerals which initially uniformly contained water with $\sim$ twice the D/H value commonly assumed for magmatic water on Mars. The curve shows the mixing model from which the initial D/H of the minerals was calculated.

of 1.90 ± 0.25 times SMOW for the D/H of the magmatic water end member. This fit assumes only that the low-D/H end member has a constant D/H value. In summary, the most straightforward interpretation of the data presented in Fig. 2 is that magmatic water is the low-D/H end-member in the mixing process represented by the analyses, and that the D/H value of this water is not the same as terrestrial water, but rather has D/H $\sim 1.9 \pm 0.25$ SMOW.

Recent ion microprobe work on *anhydrous* minerals and *secondary* clays in a nakhlite recovered from Northwest Africa after extensive exposure to the terrestrial environment (NWA 817) conflict with these previous analyses and suggest that martian water is very similar to terrestrial water in D/H value (Gillet et al., 2002). Clearly, further analyses of D/H values in martian meteorites are needed to clarify this discrepancy. However, the best suited data to address accreted water D/H ratios on Mars are those derived from analysis of magmatic hydrous minerals. Such data clearly indicate that martian magmatic D/H is elevated compared to terrestrial values.

4. Calculations for Mars

The typical outcome of the dynamical simulations leads to abundant water on the Earth, supplied during collisions of the planet-sized embryos. The planet at the position of Mars acquires large amounts of water in this fashion as well, in about 75% of the simulation. In all of the eleven simulations we analyzed, the planet roughly at the position of Mars was struck by large planetary embryos—wet or dry—and acquired too much mass. As described above, this result is obtained in more recent published simulations as well. The situation that obtained in our solar system was evidently different, and hence by hypothesis Mars could not have acquired its inventory of water by collision with another massive embryo. (There is a small possibility that Mars could have formed from the collision of two Mercury-mass embryos, but the probability that one of these would be from the water-rich region beyond 2.5 AU is extremely small, based on the aggregate behavior of the embryo accretion phase from the simulations cited above.)

However, Mars could not have avoided collision with the numerous populations of small asteroids and comets, and so we determine how much water Mars could have acquired from these populations and what the resulting isotopic composition of this water might be. To do so, we calculate the probability of collision of asteroids and comets with Mars based on the procedure described in Morbidelli et al. (2000) and consistent with the general dynamical picture sketched above. Some fraction of the roughly one Earth mass of asteroidal material present between 2.5 and 4.0 AU was in the form of large embryos, and some in the form of small asteroids. The fraction in the form of small asteroids varies in different dynamical models from 10–70%, and was certainly time dependent. Therefore, we consider a range of mass in

the form of small asteroids, in the region 2.5–4.0 AU, of 0.1–1 Earth masses.

The mean cumulative collision probability is computed with a procedure equivalent to that discussed in Morbidelli and Gladman (1998). Our numerical simulation provides the orbital elements as a function of time for each of the simulated asteroids as well as the orbital elements and mass of Mars. For every set of orbital elements as a function of time, the collision probability is computed averaging over all possible orbital configurations occurring during a precessional cycle of the orbits. For the Earth gravitational focusing is significant (Morbidelli et al., 2000), but not in the case of Mars. This procedure has been accomplished with a numerical code implemented by (Farinella and Davis, 1992) and kindly provided to us.

For comets, we assume 50 Earth masses of material in the Jupiter-Saturn region and another 50 Earth masses in the Uranus Neptune zone (we distinguish these because the collision probabilities are computed somewhat differently for the two groups as described below). We assume that the comets are 50% water ice by mass. To compute the collision probabilities with the terrestrial planets we treat the comets as test particles with semimajor axes ranging from 4.5 to 9 AU with non-regular spacing. For all test particles, the values of the angles are chosen randomly, while the eccentricities and inclinations are set equal to zero. Each test particle was followed using the "swift-rmvs3" integrator (Levison and Duncan, 1994) until it was ejected on hyperbolic orbit or entered into collision with a giant planet. Its total collision probability with Mars (assumed to be on its present orbit) is computed over the test particle's lifetime with the method discussed in Morbidelli et al. (2000). Although the calculation proceeds without explicit tracking of the embryos, we use a main belt excitation model consistent with the existence of embryos (Petit et al., 2000). For comets beyond 9 AU we use a constant collision probability computed by (Levison et al., 2000). Further details can be found in Morbidelli et al. (2000).

For asteroids, the cumulative collision probability with Mars originally in the outer belt (> 2.5 AU) is 6.4×10^{-4}, while that for the Earth is 1.3×10^{-3}. We obtain a collisional history of these asteroids with Mars as shown in Fig. 3. For comets the collision probability with Mars, averaged over 0.5 AU bins, is roughly 0.5×10^{-6} to 3×10^{-6} per particle for orbital semimajor axes of 5–8 AU, decreasing to smaller values for larger semimajor axes (Fig. 4). We assume comets are 50% water ice by mass and set the cometary D/H ratio to be twice SMOW (Meier et al., 1998) and that of water-bearing asteroids to have 10% water by mass with D/H = SMOW based on the carbonaceous chondrites.

The relative water abundances between Earth and Mars depend on the retention of water during accretion. Retention efficiency in giant impacts versus that in collisions with small comets and asteroids may be quite different since the details of the impact process differ greatly; much more detailed simulations of water loss in both types of processes are
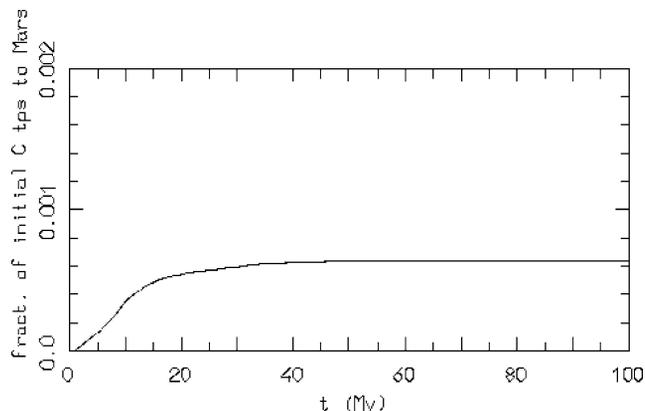

Fig. 3. Collisional history of water-laden asteroids (those bodies with initial semimajor axis between 2.5 and 4 AU), expressed as the cumulative fraction of such "C-type" asteroids accreted by Mars versus time in millions of years.
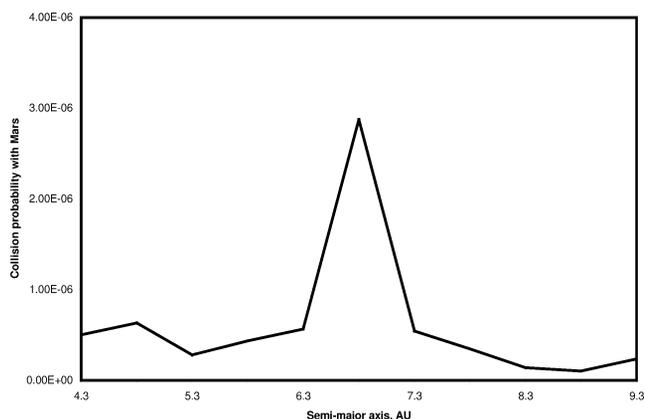

Fig. 4. Probability of collision with Mars of comets as a function of their initial semimajor axes. The calculation that generated the figure had semi-major axes binned in 0.5 AU intervals. Beyond 9.5 AU, the impact probability is taken to be constant; inward of that radius the impact probability is obtained as described in the text.

required to specify these with precision. For small asteroids and comets striking Mars at velocities greater than 15 km/s, essentially all of the expanding vapor plume will exceed the martian escape velocity of 5 km/s, and the water will be lost (Segura et al., 2002). As the impact velocity drops below this value, progressively more of the water is retained. The asteroids colliding with Mars should have had typical velocities of 12 km/s, and so we assume Mars retained most of the water acquired from asteroids. Comets had typical velocities in the 13–17 km/s range (with significant overlap between typical velocities for Jupiter–Saturn versus Uranus–Neptune comets), and hence loss of water from collision with these bodies would have been larger. To take account of this we impose a retention factor for collisions with comets of 0.5, which as shown below only modestly affects the numbers we report here.

The result of our analysis is that Mars acquires an amount of water equivalent to 0.06–0.27 Earth oceans, with a D/H ratio of 1.6 SMOW for 0.06 oceans and 1.2 SMOW for 0.27

oceans. The source of this water is split roughly evenly between comets and small asteroids for the dryer, higher-D/H value; asteroids dominate for the wetter, lower-D/H part of the range. (Were we to ignore the velocity difference between the asteroids and the comets, setting the retention factor for comets equal to unity, the range in water abundance would be 0.10–0.30 Earth oceans, with a D/H ratio of 1.8 for 0.10 oceans and 1.2 SMOW for 0.30 oceans.) Mars actually receives more water from small asteroids and comets than does the Earth, but consistent with the results in Morbidelli et al. (2000), the Earth received the bulk of its water from the large embryos rather than the small asteroids and comets.

5. Comparison of the model results to data on martian water

We find a starting value of 0.06–0.27 Earth oceans for martian water, delivered exclusively by comets and asteroids with semi-major axes greater than 2.5 AU. Converting our units (Earth oceans) into the typical units used to describe the amount of water on Mars, 0.06–0.27 Earth oceans corresponds to 600–2700-m worth of water equivalent on the martian surface (or in the crustal regolith). Geological and geomorphological estimates for the total amount of water on the martian surface and in the crust over the planet's history range upwards from 500 m (Carr, 1996; Baker, 2001). To relate this to the starting value derived above we must add to this the amount of water that was not outgassed and hence did not contribute to producing surface geological features or (see below) isotopic exchange with the atmosphere. The fraction of water outgassed is very uncertain, dependent on the timing of the delivery of water to Mars and on the importance of impact versus volcanic degassing (see, e.g., Pepin, 1991). Incompatible trace element data suggest that 50% is a reasonable estimate (H. McSween, personal communication; see also Norman, 1999). Under this assumption, 500 m of water on the martian surface corresponds to 1000 m equivalent total water accreted, consistent with the 600–2700 m equivalent we derive.

The D/H value derived, 1.2–1.6 times SMOW, is below or close to the value of 1.9 ± 0.25 SMOW measured in martian meteorite, QUE94201, discussed above. Hence, in the context of our model we would interpret D/H derived from magmatic water in QUE94201 as representing either a primordial martian value obtained from accretion of a mixture of asteroidal and cometary water, or one enhanced from the primordial value through an early hydrodynamic escape of water (Leshin, 2000). (D/H of the mantle is unaffected by extraction of magma on the scale considered in the meteorite analysis, because isotopic fractionation is extremely small at the high temperatures of magma generation.) The currently measured value of D/H in the martian atmosphere, roughly 5.5 times SMOW (Owen, 1992), is clearly a signature of the escape of water over a significant fraction of martian his-

tory, and we now address whether our model is consistent with this number.

The enrichment of deuterium over time in the martian atmosphere may occur by simple Rayleigh distillation, in which the lighter isotope (hydrogen) has a larger scale height in the poorly mixed atmosphere than does the heavier species. Thus, the lighter isotope is more abundant at altitudes where photochemical or charged-particle dissociation removes the hydrogen from the water, leading to escape. Alternatively, the photochemical dissociation of the hydrogen bond holding deuterium to the oxygen is more costly energetically due to the larger binding energy for the heavier isotope. Previous studies suggest that Rayleigh distillation is the most significant process (Donahue, 1995; Kass and Yung, 1999).

A recent model in which a surface reservoir of ice in isotopic equilibrium with the atmosphere is replenished by a larger crustal reservoir that is not in isotopic equilibrium with the atmosphere lead to losses of 60–160 m of water to achieve the current atmospheric D/H enrichment (5.5 SMOW) from an initial value of SMOW (Krasnopolsky, 2000). Other earlier workers cite losses of 80–90% of the initial water inventory to achieve the present atmospheric abundance, assuming an initial D/H in the martian water equal to SMOW. If the initial D/H is 1.6 SMOW, then the required water loss is reduced by a factor of two or more.

A reasonable estimate for the present amount of crustal water in Mars is a roughly 50-m-thick-equivalent global layer, twice the amount of ice in the polar regions derived from laser altimetry (Smith et al., 1999), and corresponding to only ∼ 2–10% of the amount accreted from comets and asteroids in our model. This is consistent with the initial inventory and isotopic composition of water from our models and the atmospheric D/H value. Indeed, the consistency extends as well to the *relationship* between the total amount of water accreted and the initial D/H ratio in our model, which are anticorrelated as required by the escape calculations.

The D/H ratio in Zagami, a recent (180-myr old) SNC meteorite, provides a more specific constraint on the original reservoir of water exchanging with the atmosphere because Zagami's D/H is approximately comparable to that in the atmosphere. A time-dependent model for the enrichment of deuterium on Mars yields a current crustal reservoir exchanging with the atmosphere between 50 and 250 m, and an original crustal reservoir between 200 and 2000 m (Donahue, 2001); if we assume a rough outgassing efficiency of 50% then the amount of water that Mars must have accreted is 0.04–0.4 oceans. These sets of numbers are broadly consistent with the results presented above.

Finally, the measured abundances of volatile elements and water in a subset of SNC meteorites suggests to some the possibility that Mars lost most of the water it accreted when oxygen in water bound with iron during core formation, releasing the hydrogen and leaving free only 0.01 Earth oceans (Dreibus and Wanke, 1987). This amount, equivalent to 100-m depth on the surface, may be marginally

enough to explain the valley networks and other fluvial features (Segura et al., 2002), but does not allow for sufficient water to fractionate the D/H value from 1.2–1.6 SMOW to 5.5 SMOW in the atmosphere today. Therefore, reaction of water with the iron during core formation must have been incomplete. This simply implies that most of the water was delivered to Mars late in its formation, that is, after it approached or attained its present mass, and core formation had already occurred. We see no timescale problem, because Mars did not grow by accretion of multiple giant embryos in the way the Earth did (see discussion above). Therefore, growth of Mars as its own "Mars-sized embryo" could have been essentially finished before bulk of the Earth's growth was complete; this is consistent with the recent isotopic evidence (Hf–W) that constrains core formation timescales in the Earth and Mars (Kleine et al., 2002; Yin et al., 2002). The impacts of small asteroids and comets constituted a "late veneer" which added water to Mars, in contrast to the picture for Earth where water was added through collisions with Mercury-sized embryos throughout a growth period of some tens of millions of years (Cameron, 2002).

6. Comparison with the local source hypothesis

Alternative to the "distal source" model we present here is the hypothesis that both the Earth and Mars acquired their water from local planetesimals in a cold nebula (Drake and Righter, 2002). Indeed, should such a "local source" model turn out to be correct for the Earth, it would almost certainly imply that at least as much water was available in martian planetesimals as was available in terrestrial planet-building material. In such a view, Mars could have begun its history wetter than in the distal source model we present, perhaps significantly so, and there would be no *a priori* reason to expect the starting D/H ratio of martian water to differ from that of the Earth. Most geochemists would argue that the Earth possessed at least several oceans worth of water in its mantle and crust after accretion (Abe et al., 2001)—irrespective of whether that water was accreted locally or from distal sources. Under the local source hypothesis, this number reflects the fraction of water contained in local planetesimals ($\sim 10^{-3}$ by mass) in the region of formation of Earth and Mars. Then Mars should have acquired at least 0.4 oceans worth of water, *added to* the 0.06 to 0.27 oceans worth we calculate were accreted from asteroids and comets in our distal source model.

It is difficult at present to rule out one of the two models with the available geological and geochemical data (we do not, here, attempt to argue the various compositional lines of evidence in meteorites for or against either model). Planned missions to Mars in the coming decade may provide the data required. Additional measurements of D/H in SNC meteorites of various ages, both in the current meteorite collection and those yet to be discovered, could ultimately provide

a history of isotopic enrichment of martian water that would better constrain the initial water abundance and D/H value. Finally, improved dynamical simulations of planet formation are required to help refine and clarify the probabilities that large embryos from the asteroid belt hit the Earth but not Mars.

Our work well illustrates that planetary accretion is a stochastic process, especially if much of the mass is contained in a small number of large embryos. If embryos formed in the asteroid belt, each of the inner planets could have been hit by a different number of embryos (including zero). Each planet would then have had differing amounts of volatiles delivered, and from different source regions. If this view is valid, then it implies that terrestrial planets in the CHZ around other stars may have vastly different amounts of water one from the other, and that the timing of formation and location of giant planets from one system to another could play an important role in this variation (Lunine, 2001).

References

Abe, Y., Drake, M., Ohtani, E., Okuchi, T., Righter, K., 2001. Water in the early Earth. In: Righter, K., Canup, R. (Eds.), Origin of the Earth and the Moon. Univ. of Arizona Press, Tucson, p. 1.

Baker, V.R., 2001. Water and the martian landscape. Nature 412, 228–236.

Balsiger, H., Altwegg, K., Geiss, J., 1995. D/H and $^{18}O/^{16}O$ ratio in the hydronium ion and in neutral water from in situ ion measurements in Comet P/Halley. J. Geophys. Res. 100, 5834.

Bockelée-Morvan, D., Gautier, D., Lis, D.C., Young, K., Keene, J., Phillips, T.G., Owen, T., Crovisier, J., Goldsmith, P.F., Bergin, E.A., Despois, D., Wooten, A., 1998. Deuterated water in Comet C/1996 B2 (Hyakutake) and its implications for the origin of comets. Icarus 133, 147–162.

Cameron, A.G.W., 2002. Birth of a Solar System. Nature 418, 924–925.

Carr, M.H., 1996. Water on Mars. Oxford Univ. Press, New York.

Cassen, P., 1994. Utilitarian models of the solar nebula. Icarus 112, 405–429.

Chambers, J.E., Cassen, P., 2002. Planetary accretion in the inner Solar System: dependence on nebula surface density profile and Giant Planet eccentricities. In: Proc. Lunar Planet. Sci. Conf. 33rd. Abstract 1049.

Chambers, J.E., Wetherill, G.W., 1998. Making the terrestrial planets: N-body integrations of planetary embryos in three dimensions. Icarus 136, 304–327.

Donahue, T.M., 2001. Special feature: pre-global surveyor evidence for martian ground water. Proc. Nat. Acad. Sci. 98, 827–830.

Donahue, T.M., 1995. Evolution of water reservoirs on Mars from D/H ratios in the atmosphere and crust. Nature 374, 432–434.

Drake, M.J., Righter, K., 2002. What is the Earth made of? Nature 416, 39–44.

Dreibus, G., Wanke, H., 1987. Volatiles on Earth and Mars: a comparison. Icarus 71, 225–240.

Farinella, P., Davis, D., 1992. Collision rates and impact velocities in the main asteroid belt. Icarus 97, 111–123.

Gillet, P., Barrat, J.A., Deloule, E., Wadhwa, M., Jambon, A., Sautter, V., Devouard, B., Neuville, D., Benzerara, K., Lesourd, M., 2002. Aqueous alteration in the Northwest Africa 817 (NWA 817) martian meteorite. Earth Planet. Sci. Lett. 203, 431–444.

Hoefs, J., 1997. Stable Isotope Geochemistry. Springer, Berlin.

Kass, D.M., Yung, Y.L., 1999. Water on Mars: isotopic constraints on exchange between the atmosphere and surface. Geophys. Res. Lett. 26, 3653–3656.

Kleine, T., Münker, C., Mezger, K., Palme, H., 2002. Rapid accretion and early core formation on asteroids and the terrestrial planets from Hf–W chronometry. Nature 418, 952–955.

Kominami, J., Ida, S., 2002a. The effect of tidal interaction with a gas disk on formation of terrestrial planets. Icarus 157, 43–56.

Kominami, J., Ida, S., 2002b. The effect of dissipating gas disk on terrestrial planet formation. In: American Astronomical Society, Division on Dynamical Astronomy Meeting 33rd, 12.04, Abstract.

Krasnopolsky, V., 2000. On the deuterium abundance of Mars and some related problems. Icarus 148, 597–602.

Leshin, L.A., 2000. Insights into martian water reservoirs from analyses of martian meteorite QUE94201. Geophys. Res. Lett. 27, 2017–2020.

Levison, H., Duncan, M., 1994. The long-term behavior of short-period comets. Icarus 108, 18–36.

Levison, H., Duncan, M., Zahnle, K., Holman, M., Dones, L., 2000. Planetary impact rates from ecliptic comets. Icarus 143, 415–420.

Lunine, J.I., 2001. The occurrence of jovian planets and the habitability of planetary systems. Proc. Nat. Acad. Sci. USA 98, 809–814.

Meier, R., Owen, T.C., Matthews, H.E., Jewitt, D.C., Bockelée-Morvan, D., Biver, N., Crovisier, J., Gautier, D., 1998. A determination of the HDO/H_2O ratio in Comet C/1995 O1 (Hale–Bopp). Science 279, 842–844.

Morbidelli, A., Chambers, J., Lunine, J.I., Petit, J.M., Robert, F., Valsecchi, G.B., Cyr, K.E., 2000. Source regions and timescales for the delivery of water on Earth. Meteor. Planet. Sci. 35, 1309–1320.

Morbidelli, A., Gladman, B., 1998. Orbital and temporal distributions of meteorites originating in the asteroid belt. Meteor. Planet. Sci. 33, 999–1016.

Norman, M.D., 1999. The composition and thickness of the crust of Mars estimated from rare Earth elements and neodymium-isotopic compositions of martian meteorites. Meteor. Planet. Sci. 34, 439–449.

Owen, T., 1992. The composition and early history of the atmosphere of Mars. In: Kieffer, H.H., Jakosky, B.M., Snyder, C.W., Matthews, M.S. (Eds.), Mars. Univ. of Arizona Press, Tucson, pp. 818–834.

Pepin, R.O., 1991. On the origin and early evolution of terrestrial planet atmospheres and meteoritic volatiles. Icarus 92, 2–79.

Petit, J.M., Morbidelli, A., Chambers, J., 2000. The primordial excitation and clearing of the asteroid belt. Icarus. In press.

Robert, F., 2001. The origin of water on Earth. Science 293, 1056–1058.

Robert, F., Gautier, D., Dubrulle, B., 2000. The Solar System D/H ratio: observations and theories. Space Sci. Rev. 92, 201–224.

Rubin, A.E., Warren, P.H., Greenwood, J.P., Verish, R.S., Leshin, L.A., Hervig, R.L., Clayton, R.N., Mayeda, T.K., 2000. Insights into martian water reservoirs from analyses of martian meteorite QUE94201. Geophys. Res. Lett. 27, 2017–2020.

Segura, T.L., Toon, O.B., Colaprete, A., Zahnle, K., 2002. Environmental effects of large impacts on Mars. Science 298, 1977–1980.

Smith, D.E., Zuber, M.T., Solomon, S.C., Phillips, R.J., Head, J.W., Garvin, J.B., et al., 1999. The global topography of Mars and implications for surface evolution. Science 284, 1503.

Sugiura, N., Hoshino, H., 2000. Hydrogen-isotopic compositions in Allan Hills 84001 and the evolution of the martian atmosphere. Meteor. Planet. Sci. 35, 297.

Watson, L.L., Hutcheon, I.D., Epstein, S., Stolper, E.M., 1994. Water on Mars: clues from deuterium/hydrogen and water contents of hydrous phases in SNC meteorites. Science 265, 86–90.

Yin, Q., Jacobsen, S.B., Yamashita, K., Blichert-Toft, J., Télouk, P., Albaréde, F., 2002. A short timescale for terrestrial planet formation from Hf–W chronometry of meteorites. Nature 418, 949–952.