

## Source regions and timescales for the delivery of water to the Earth

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**Abstract**—In the primordial solar system, the most plausible sources of the water accreted by the Earth were in the outer asteroid belt, in the giant planet regions, and in the Kuiper Belt. We investigate the implications on the origin of Earth's water of dynamical models of primordial evolution of solar system bodies and check them with respect to chemical constraints. We find that it is plausible that the Earth accreted water all along its formation, from the early phases when the solar nebula was still present to the late stages of gas-free sweepup of scattered planetesimals. Asteroids and the comets from the Jupiter–Saturn region were the first water deliverers, when the Earth was less than half its present mass. The bulk of the water presently on Earth was carried by a few planetary embryos, originally formed in the outer asteroid belt and accreted by the Earth at the final stage of its formation. Finally, a late veneer, accounting for at most 10% of the present water mass, occurred due to comets from the Uranus–Neptune region and from the Kuiper Belt. The net result of accretion from these several reservoirs is that the water on Earth had essentially the D/H ratio typical of the water condensed in the outer asteroid belt. This is in agreement with the observation that the D/H ratio in the oceans is very close to the mean value of the D/H ratio of the water inclusions in carbonaceous chondrites.

### INTRODUCTION

The origin of water on Earth remains one of the most important subjects of debate and controversy in solar system formation science. It is well known that the meteorites show a gross correlation between their water content and their original heliocentric distance: carbonaceous chondrites, from the outer asteroid belt (2.5–4 AU), are water rich (up to 10% in mass), whereas ordinary and enstatite chondrites, from the innermost part of the asteroid belt (~2 AU), are the driest known meteorites in the solar system (0.05–0.1% in mass). This suggests that the planetesimals formed in the Earth's zone should have had an even lower water content, attributable to the higher temperatures at which the grains accreted. In addition, a non-negligible fraction of their water should have been lost in the Earth's accretion process. Therefore, the prevailing opinion is that the water presently on Earth came from the outer solar system, carried by comets colliding with the freshly-formed Earth (see Owen and Bar-Nun, 1995). This is usually called the late veneer scenario.

However, recent astronomical and geochemical analyses have raised serious doubts regarding the cometary late veneer scenario. The terrestrial D/H ratio has been accurately estimated (Lécuyer *et al.*, 1998) to be ~6× higher than the protosolar value (Mahaffy *et al.*, 1998). This ratio is believed to have been essentially unaltered by hydrothermal circulation in the Earth's crust over time—on the basis of the lack of a large reservoir of H with which to exchange the D—so that it should be diagnostic of the isotopic composition of the planetesimals that delivered the water to the Earth. The D/H ratio has been measured only in three comets: Halley (Balsiger *et al.*, 1995; Eberhardt *et al.*, 1995), Hale–Bopp (Meier *et al.*, 1998), and Hyakutake (Bockelée-Morvan *et al.*, 1998), and in all cases it turned out to be ~12× higher than the protosolar value, and twice the enrichment characterizing the Earth's water. Even taking into account the percentage of error (15% uncertainty for Halley, 30% for the others), it appears that comets of this kind could not have

been the dominant source of Earth's water. These comets are believed to come from the Oort Cloud, itself populated mostly by planetesimals that were originally in the Uranus–Neptune region and in the primordial Kuiper Belt (Duncan *et al.*, 1987; Hahn and Malhotra, 1999), so that their high D/H ratio should be typical of all icy planetesimals formed in the outer solar system. According to the nebular model by Drouart *et al.* (1999), the Jupiter–Saturn region and the outer asteroid belt should be the only regions where planetesimals could have included water with essentially the isotopic composition of that of the Earth. This conclusion is partially confirmed by data: the D/H ratio in the OH radicals in the hydrous carbonaceous meteorites, which are believed to come from the outer asteroid belt, is measured to be on average very similar to that on Earth; unfortunately, no measure of the D/H ratio for the Trojan asteroids (the only surviving planetesimals from the Jupiter–Saturn region) is yet available.

In addition, the high degree of oxidation of the Earth's mantle seems to suggest that a small amount of water was already present during the early phases of Earth's formation. This has long been considered to be in contradiction with the known partitioning of the siderophile elements between Earth's core and mantle, which geochemists could only account for by assuming the absence of water. However, Righter and Drake (1999) have recently shown that the amount of water required for the iron oxidation does not contradict the existing geophysical models, thus lending support to the idea that water could have been accreted by the Earth much earlier than the late veneer.

These new results suggest that it is timely to revisit the astronomical models for the delivery of water to the Earth. Therefore, we have quantitatively analyzed the contributions from the major reservoirs of water, in the context of the most plausible existing scenarios of planet formation and primordial evolution of the solar system. We start (see below) by reviewing the chemical data on water and rare gases on Earth and in carbonaceous

meteorites and comets. Then, the following section is devoted to the study of the delivery of material from the asteroid belt, during its primordial mass depletion phase, based upon a model recently developed by Chambers and Wetherill (1998) and Petit *et al.* (unpubl. data, 2000). However, alternative models on the primordial depletion and dynamical excitation of the asteroid belt have been recently proposed, so that next we discuss their implications for the origin of Earth's water. Finally, we consider the contribution of comets, separately for those initially in the Jupiter–Saturn zone and for those from regions further out in the solar system.

For each reservoir and each model, we compute the efficiency and the characteristic timescale for the delivery of material to the growing Earth. For this purpose, we assume that the Earth was formed by high velocity collision of massive planetary embryos on a timescale of several  $10^7$ – $10^8$  years, according to the simulations by Chambers and Wetherill (1998) and Agnor *et al.* (1999), although the formation of Jupiter and the dissipation of the planetary nebula are completed within  $\sim 10$  Ma. The exact chronology is not important here, the only relevant property being that the growth of the Earth takes much longer than the formation of Jupiter and the dissipation of the planetary nebula.

In Comparison of Geochemical Data, we will discuss the compatibility of our results with the isotopic composition of Earth's water. We will also briefly discuss the rare gas problem and suggest a possible interpretation to be further investigated. In Conclusions we summarize the results as a chronology of the accretion of water by the growing Earth.

#### VOLATILE ELEMENTS INVENTORY

A summary of well-established geochemical data for the volatile elements on Earth and in carbonaceous chondrites and comets is presented in Table 1.

The mass of the water contained in the Earth's crust (including the ocean and the atmosphere) is estimated to be  $1.7 \times 10^{24}$  g, namely  $2.8 \times 10^{-4}$  Earth masses ( $M_{\oplus}$ ). The mass of the water in the present-day mantle is estimated to be in the range of  $(0.8\text{--}8) \times 10^{-4} M_{\oplus}$  (Lécuyer *et al.*, 1998), so that a conservative value of  $\sim 5 \times 10^{-4} M_{\oplus}$  can be assumed for the total mass of water on Earth. However, an unknown additional amount of water could have resided in the primitive Earth's mantle, estimates ranging up to the equivalent of 50 Earth ocean masses of water (Abe *et al.*, 2000). In the following investigation of the source of the Earth's water, we will assume  $5 \times 10^{-4} M_{\oplus}$  as a nominal value of the amount of water that must have been supplied to the Earth.

The D/H ratio in the present-day mantle is close to that of the water in the ocean; as said in the Introduction, it is  $\sim 6\times$  higher than the solar value (for molecular H), and about half of that found in comets. The carbonaceous chondrites have a mean D/H ratio (averaged over all known samples) of  $(1.59 \pm 0.1) \times 10^{-4}$  (Dauphas *et al.*, 2000), that is very similar, although not exactly equal, to that of the Earth. However, the D/H ratios of the individual carbonaceous chondrites range over the interval  $(1.28\text{--}1.80) \times 10^{-4}$ , so that the D/H ratio of the terrestrial water is well within the chondritic values. For this reason, the D/H ratio on Earth is generally said to be "chondritic". Strictly speaking, this does not imply that the water on Earth has been carried by carbonaceous chondrites.

As H in the form of water is continuously recycled in the deep mantle, the D/H ratio of the primitive Earth mantle cannot be precisely known. Data on deep mantle rocks indicate that this D/H ratio should be  $< 1.38 \times 10^{-4}$  (Deloule *et al.*, 1991), that is definitely smaller than that of comets; on the other hand, it is difficult to imagine that its value could have been smaller than the minimum D/H ratio found in carbonaceous chondrites ( $1.28 \times 10^{-4}$ ; Kerridge, 1985).

In the case of Ne, no important recycling is expected between surface and mantle reservoirs (Sarda *et al.*, 1988; Marty, 1989). Thus, the isotopic compositions of these two reservoirs can be regarded as face values for the primitive Earth. Note that the Ne in the deep Earth has an isotopic composition close to solar. Conversely, its surface value is more similar to chondritic: this could indicate either that the bulk of atmospheric Ne has been delivered by carbonaceous chondritic planetesimals or that a large part of the primordial Ne—with a solar isotopic composition—has been lost into space yielding an important isotopic fractionation of the remaining part.

The Xe-isotopic composition (not reported in Table 1) is mass-dependently fractionated with the heavy isotopes enhanced in the atmosphere by 3% per amu compared with solar and chondritic compositions (Pepin 1991).

In Comparisons of Geochemical Data, we will evaluate our dynamical models for the delivery of water, presented next, with respect to these data.

#### DELIVERY OF WATER DURING THE DEPLETION OF THE PRIMORDIAL ASTEROID BELT: MODEL I

If most of the Earth's water has been delivered by hydrated carbonaceous asteroids, even assuming a 100% efficiency in the impact delivery (*i.e.*, a negligible fraction of water is lost to space at the moment of the impact) and a 10% water concentration of these

TABLE 1. Geochemical data for some volatile elements.

Object*	H <sub>2</sub> O (ppm)	Ne (mol/g; $\times 10^{-13}$ )	Xe (mol/g; $\times 10^{-16}$ )	D/H ( $\times 10^{-6}$ )	<sup>20</sup> Ne/ <sup>22</sup> Ne
Mantle†	80–800	–	–	145	13.2
Atm.+Sed.‡	280	5.00	1.1	153	9.80
Bulk§	360–1080	–	–	$149 \pm 3$	–
C.C.#	$1 \times 10^5$	160–250	300–500	128–180	8.9–9.6
Comets§	$5 \times 10^5$	–	–	$309 \pm 20$	–
Protosolar@	–	–	–	$25 \pm 5$	13.8

\*Atm.+Sed. stands for atmosphere and sediments (including the ocean) and C.C stands for carbonaceous chondrites. The abundances of water, Ne, and Xe in the mantle and in Atm.+Sed. are expressed as concentrations with respect to the total mass of the Earth.

†Kerridge (1985), Sarda *et al.* (1988), Deloule *et al.* (1991), Franchi *et al.* (1993), Cartigny *et al.* (1997, 1998).

‡Ozima and Podosek (1983), Marty and Humbert (1997), Lécuyer *et al.* (1998).

§Kyser and O'Neil (1984), Bell and Rossman (1992), Marty (1995), Marty and Humbert (1997), Lécuyer *et al.* (1998).

#Boato (1954), Mazor *et al.* (1970), Kerridge (1985), Robert and Epstein (1982).

§Jessberger *et al.* (1988), Meier *et al.* (1998), Bokelée-Morvan *et al.* (1998).

@Geiss and Gloecker (1998).

impacting bodies (comparable to the most hydrated carbonaceous meteorites, see Table 1), it turns out that at least  $5 \times 10^{-3} M_{\oplus}$  of carbonaceous material should have been accreted by the Earth. This is roughly  $10\times$  more than the current mass of the entire asteroid belt.

Thus, the delivery of water from the region of the asteroid belt could have been significant for Earth's water inventory only during the period when the primordial belt was undergoing a substantial depletion. Two lines of evidence show that the asteroid belt must have been  $(10^2\text{--}10^3)\times$  more massive in the past: the reconstruction of the primordial surface density by interpolation of the solid material incorporated in the planets (Weidenschilling 1977), and the accretion of the largest asteroids on a timescale comparable with the meteoritic solidification age (Wetherill 1989). The mass loss cannot be explained by invoking an intense primordial collisional activity in the asteroid belt, because otherwise the fragile basaltic crust of Vesta would not have survived (Davis *et al.*, 1994). Therefore, the most plausible explanation is that most of the bodies have been somehow scattered from what is identified today as the asteroid belt region.

Unfortunately, there is not a unanimous consensus on how and when the expulsion of most of the material from the asteroid belt

occurred. In this section, we study the implications of a model originally proposed by Wetherill (1992), and more fully elaborated by Chambers and Wetherill (1998) and Petit *et al.* (unpubl. data, 2000). This model is one that best explains the presently observed characteristics of the asteroid belt. The basic idea is that the runaway process that led to the formation of planetary embryos was not restricted to the terrestrial planet region (semimajor axis  $a < 2$  AU) and Jupiter's region (a massive Jovian core at  $\sim 5$  AU), but also occurred in the asteroid belt ( $2 < a < 4$  AU). It is therefore assumed that lunar to martian mass planetary embryos, separated by a few mutual Hill's radii, formed all over the inner solar system ( $a < 4$  AU). What is typically observed in the simulations of such a system is shown in Fig. 1 and can be described as follows (for the details and discussion of the simulation technique see Chambers and Wetherill, 1998). The embryos start on quasi-circular and coplanar orbits, with a mass vs. semimajor axis distribution shown in Fig. 2c. 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 each

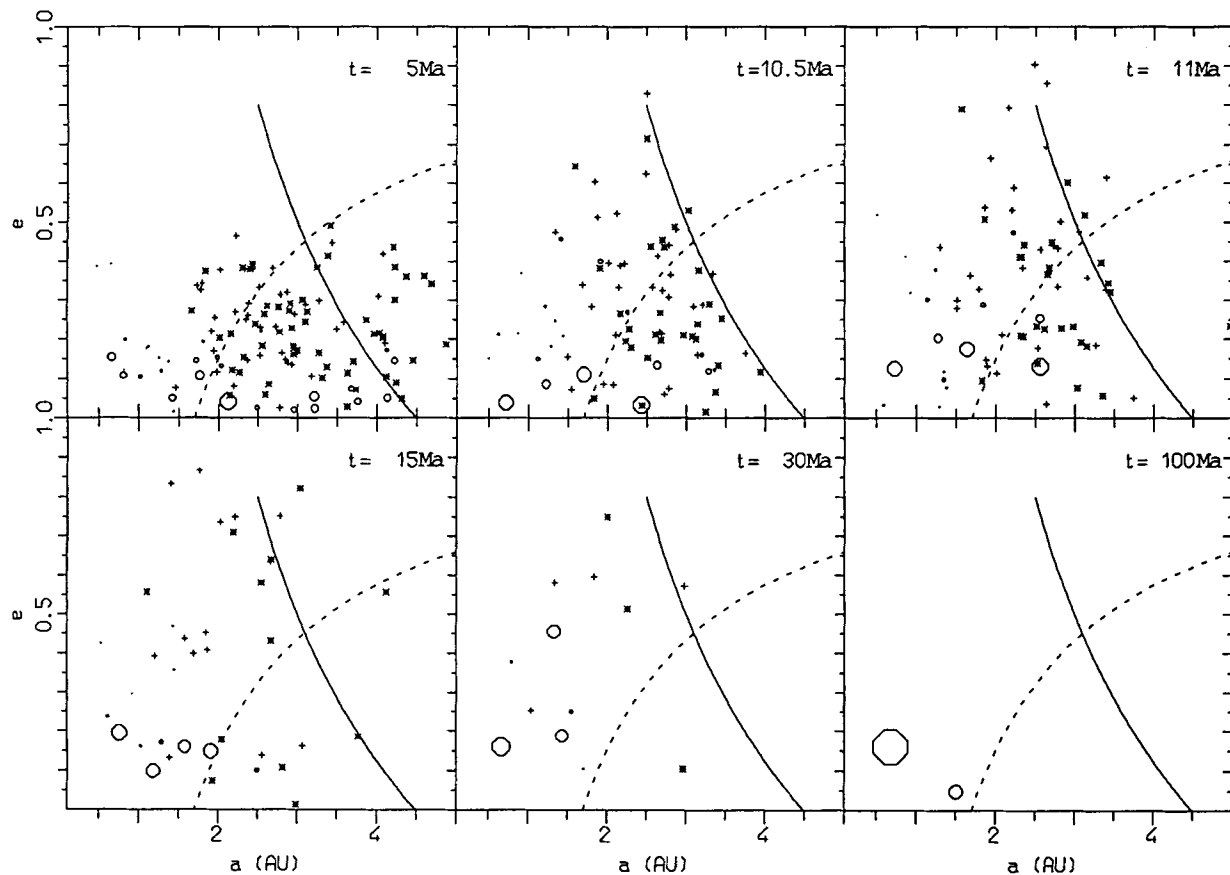


FIG. 1. Snapshots of the orbital distribution of the asteroids and of the planetary embryos. Asteroids are denoted by crosses if their initial semimajor axis was between 2 and 2.5 AU, and by asterisks if their initial semimajor axis was beyond 2.5 AU. The embryos are denoted by open circles, whose size is linearly proportional to their mass. Initially both embryos and asteroids have quasi-circular and coplanar orbits. The initial mass distribution of the embryos is shown in Fig. 2c. The solid and dash curves refer to  $Q = 4.5$  AU and  $q = 1.7$  AU and basically mark the boundaries of the present-day asteroid belt. A full-mass Jupiter is introduced in the simulation at 10 Ma. Notice that before 10 Ma the asteroids orbits are excited, but just a few asteroids are outside the boundaries of the present-day belt. Only a minority of those with initial semimajor axis beyond 2.5 AU reaches small semimajor axis. When Jupiter is introduced, the excitation becomes larger, and the belt is rapidly depleted. At 30 Ma there is just one asteroid out of 100 left in the belt, and at 100 Ma no asteroids are left. The complete depletion of the belt is an artifact of the limited number of integrated asteroids (100). In fact, Petit *et al.* (unpubl. data, 2000) find that seven asteroids out of 1000 stay in the belt at the end of the simulation. At 100 Ma, two terrestrial planets are left, in stable configurations. The largest planet has a mass equal to  $1.39 M_{\oplus}$  and a semimajor axis of 0.7 AU; we refer to this object as the "Earth". The smallest one has almost exactly Mars' orbit, but has a mass equal to half an Earth mass.

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 (see the panel at  $t = 5$  Ma in Fig. 1).

As Jupiter accretes its gaseous component and approaches its current mass, (for concreteness consider that this happens after 10 Ma, but the exact timing is not important), the dynamical evolution of the system changes abruptly, because the distant perturbations of the giant planet become effective, and powerful mean motion 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 in one of these resonances, thereby acquiring larger eccentricities. As a consequence, the embryos initially in the asteroid belt have three possible fates (in order of decreasing likelihood): (1) They intersect Jupiter's orbit and are rapidly ejected on hyperbolic orbits; (2) They cross the orbits of the embryos in the  $a < 2$  AU region, and are accreted by the latter on a longer timescale; (3) Their eccentricity is pumped to unity by some resonance with Jupiter and they therefore collide with the Sun. The same does not happen to the embryos with  $a < 2$  AU: because of the small semimajor axes, they cannot encounter Jupiter and be ejected; moreover, in their region the resonant perturbations of Jupiter are much less effective than in the asteroid belt. Therefore, at the end of the simulation (see panel at  $t = 100$  Ma in Fig. 1f) the asteroid belt is cleared of embryos, whereas in the  $a < 2$  AU region a few planets with masses comparable to that of the Earth have been formed.

The asteroids, whose initial orbits are also circular and coplanar, share a similar fate. Having encounters with the embryos, most of them fall into one of the resonances, and therefore escape to very large eccentricities. By the time that all embryos leave the belt, typically only 1% of the initial asteroids survive at low to moderate eccentricities in the Petit *et al.* (unpubl. data, 2000) simulations. Notice that in Fig. 1 no asteroids seem to survive in the main belt region. This is an artifact of the limited number of initial asteroids shown in the plot (100). In fact, Petit *et al.* find that 7 asteroids out of 1000 stay in the belt at the end of the simulation shown here. The elimination of all the embryos and of ~99% of the small bodies therefore explains the strong mass deficit of the remaining asteroid belt population. Not everything in these simulations is fully consistent with the present architecture of our planetary system. The inner asteroid belt ( $a < 2.8$  AU) is too severely depleted with respect to its central part ( $2.8 < a < 3.3$  AU); typically only two terrestrial planets survive at the end of the simulation (although 4 simulations out of 11 produce three planets), and they have a final eccentricity and inclination larger than those observed (the latter explains the former: being more eccentric, our planets require to be more mutually separated in order to be stable, which leaves room for only two of them). The planet formed in the Mars zone typically has a mass much larger than that of Mars. Despite all of these limitations, we believe that this model provides the most satisfactory reconstruction of the formation of the terrestrial planets and of the depletion of the asteroid belt available at present.

In the framework of this model, water would be delivered to the forming Earth both by planetary embryos and by asteroids originally located far enough from the Sun. We consider 2.5 AU to be a good

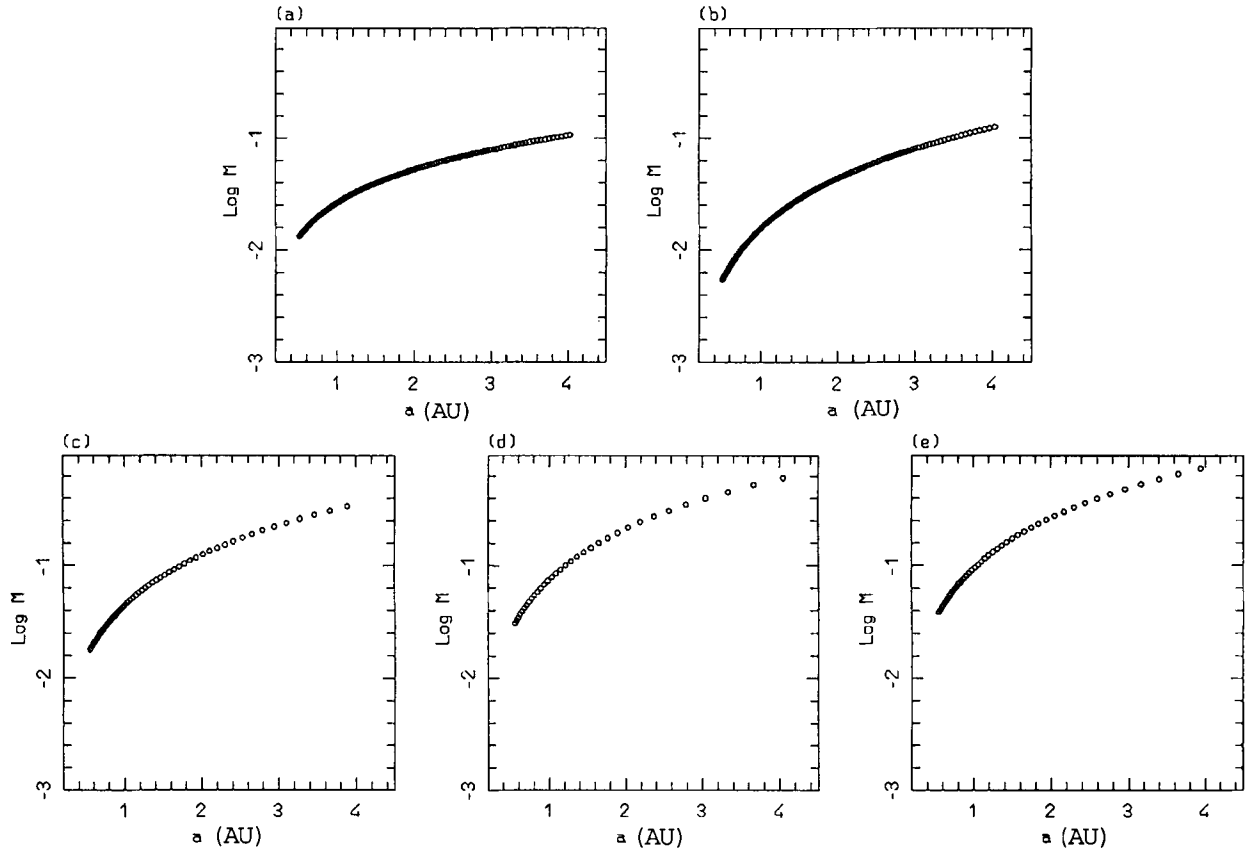


FIG 2. The initial mass distribution of the planetary embryos in the different simulations.  $M$  is expressed in Earth masses. The total mass is  $6.6 M_{\oplus}$  in (a) and (b),  $5.0 M_{\oplus}$  in (c),  $5.5 M_{\oplus}$  in (d) and  $8.6 M_{\oplus}$  in (e).

threshold distance for the location of water-rich bodies. In fact, the models of Cyr *et al.* (1998) show that meter-sized water-ice planetesimals could have drifted inward from a condensation front for water ice (hereafter called the "snowline"), lying roughly at  $\sim 5$  AU. The limited surface area of these bodies would have inhibited loss of water by sublimation outside of roughly 3 AU. Thus, inward of this point, a local maximum of water vapor might have been available for hydration reactions, and outward of that point meter-sized snowballs could have been swept up by the growing bodies. Of course, the nebular environment and hence location of the snowline, and the history of water trapped therein, is strongly time-dependent (Drouart *et al.*, 1999). Observations show that C-type (carbonaceous, water-rich) asteroids dominate the present asteroid belt population beyond 2.5 AU, while the bodies inside 2.5 AU are in the majority S-type (water-poor bodies).

Below, we quantify the transport of water, separately for embryos and asteroids originally beyond 2.5 AU.

### Water from Primitive Planetary Embryos

For statistical purposes, we have analyzed 11 simulations similar to that of Fig. 1, where terrestrial planets are formed from a population of planetary embryos ranging from 0.5 to 4 AU. All these simulations have been done using the Mercury integrator, written by J. Chambers, and nine of them have been presented already in Chambers and Wetherill (1998). (These nine integrations were done using a preliminary version of the Mercury integrator, which was not symplectic.) Figure 2 shows the initial distribution of the embryos in terms of mass vs. semimajor axis. In all cases, the mass of the embryos is an increasing function of the semimajor axis. The rationale for this is that the runaway growth of an embryo should stop when the embryo has accreted most of the mass available in an annulus of width comparable to its Hill's radius. The Hill's radius of a body of mass  $M$  at heliocentric distance  $a$  is:

$$R_H = a \left( \frac{M}{3M_\odot} \right)^{1/3} \quad (1)$$

where  $M_\odot$  is the mass of the Sun. The mass available in an annulus of width  $R_H$  and radius  $a$  is

$$M = 2\pi a R_H \sigma \quad (2)$$

where  $\sigma$  is the disk's surface density of solid material. Substituting (1) into (2) and solving for  $M$ , one gets that the mass of an embryo at the end of its runaway growth should be proportional to  $\sigma^{3/2} a^3$ . The surface density  $\sigma$  is usually assumed to be between  $1/a$  and  $1/a^{3/2}$ , so that the masses of the embryos are expected to grow with semimajor axis as a function between  $a^{3/2}$  and  $a^3$ . Four of the five distributions shown in Fig. 2 follow an  $a^{3/2}$  law, whereas in the first distribution the mass of the embryos grows linearly with  $a$ . The formation by runaway growth of a Jupiter's core of a few Earth masses at  $\sim 5$  AU also argues for a mass of the embryos that increases with the semimajor axis.

All of the 11 simulations that we have analyzed lead to the formation of a planet of mass comparable to that of the Earth in the terrestrial planet region (see Fig. 1f for the end state of one of the simulations that starts from the distribution of Fig. 2c). We call this planet an Earth. In some cases (see for instance Fig. 1), the final position of the Earth-mass planet is closer to the real one of Venus

than to that of the Earth. From the point of view of the present model of chaotic planetary formation, ending at 0.7 AU or 1 AU is just a matter of chance. We thus consider all such planets as reproductions of our Earth. In all simulations, the Earth has accreted at least one embryo initially located beyond 2.5 AU. By analogy with the composition of the asteroids in the same region, these embryos should have been C-rich, and probably heavily hydrated; moreover the D/H ratio of their water should have been similar to that of the water included in the carbonaceous chondrites (see Volatile Elements Inventory). For convenience, in the following, we will refer to these embryos as primitive, simply to distinguish them as water- and C-rich bodies relative to planetesimals closer to 1 AU (with no implication regarding their final location).

Therefore, our simulations suggest that the accretion of water with a terrestrial D/H ratio is a natural byproduct of the Earth's accretion. Table 2 summarizes in detail the results of each simulation, as far as the accretion of primitive material is concerned.

As shown in Table 2, there is an apparent correlation between the initial mass distribution of the embryos and the fraction of accreted primitive mass. The two simulations that started with the embryos distributions shown in Fig. 2a,b produced an Earth for which  $\sim 10\%$  of the mass has been brought by embryos originally beyond 2.5 AU. The three simulations starting with the distribution of Fig. 2c produced an Earth for which 15–20% of the mass is carbonaceous. These results are compatible with classical geochemical models, in which the Earth is built from  $\sim 15\%$  carbonaceous-chondrite-like material and  $\sim 85\%$  ordinary-chondrite-like material (Ringwood, 1979; Wanke, 1981). Moreover in all these simulations, the primitive embryos are always accreted at late times, when the Earth has already acquired a substantial fraction of its final mass.

Conversely, the six simulations that started with the embryos distributions shown in Fig. 2d,e produced an Earth for which a much larger fraction of the mass has been brought by embryos originally beyond 2.5 AU. In five of these simulations, the mass of primitive material in the Earth is larger than 25% of the total mass (this is no surprise because of the very large initial mass of the primitive embryos in these simulations). Such large fractions are hardly compatible with geochemical data. Moreover, for four simulations, the fourth column of Table 2 indicates  $T = 0$ . This means that a primitive embryo has played the role of accretion seed. The notion of accretion seed requires some explanation. When two embryos, A

TABLE 2. Summary of the results of 11 simulations of Earth's accretion.\*

Embros dist.	$N(a > 2.5 \text{ AU})$	$M(a > 2.5 \text{ AU})$	$T$ at accretion	$M$ at accretion
a	2	9%	68.5	100%
b	2	12%	82.9	85%
c	1	17%	34.0	96%
c	1	15%	65.3	68%
c	1	21%	46.8	90%
d	1	11%	121.1	78%
d	1	25%	0	–
d	3	47%	0	–
e	1	49%	0	–
e	1	36%	106.3	100%
e	1	35%	0	–

\*The first column reports which panel of Fig. 2 shows the corresponding initial distribution of the embryos; the second column indicates the number of embryos originally located beyond 2.5 AU that are accreted by the Earth; the third column shows which fraction of the final mass of the Earth has been accreted from these presumably primitive embryos; the fourth entry gives the time (in millions of years) at which the last primitive embryo is accreted (when the time is 0 it means that the primitive embryo has played the role of "accretion seed"—see text for definition); the fifth column shows what fraction of its final mass the Earth has attained with the accretion of the last primitive embryo.

and B, collide, if the mass of A is larger than the mass of B we say that "A accretes B". A new embryo carrying the sum of the masses is created at the position of the barycenter of A and B, with a speed such that the linear momentum of the A+B system is conserved. The newly formed planetesimal inherits the name A, whereas B disappears from the simulation. As a consequence, at the end of the simulation, the Earth carries the name of the embryo that has always been the largest in all binary collisions. We call this embryo the accretion seed. It is unclear if the presently observed structure of the Earth, whose volatile chemistry becomes similar to that of carbonaceous chondrites only for upper mantle samples, is compatible with a primitive embryo playing the role of accretion seed.

We think that the scenario of the delivery of water by embryos formed in the outer asteroid belt has several merits. First, it is not an *ad hoc* scenario: It is the natural implication of a model that explains in a unified way the accretion of terrestrial planets as well as the excitation and the depletion of the asteroid belt. Second, it accounts for the delivery of a large amount of water having a similar D/H ratio to that in the water of carbonaceous chondrites, and hence the same D/H ratio as in oceanic water. Third, this delivery happens late in the Earth's formation—so that water could be retained—but still during planetary growth.

On the other hand, there are several possible objections to this model: (1) The results reported above rely on a few impacts of primitive embryos in each simulation (see column 2 of Table 2), so that they could suffer from small number statistics problems. In fact, the small number of impacts is not an artifact of the simulation; if the present model is correct, the delivery of water would occur in one or a few impacts. This implies the potential for a large variation in volatile inventory from one terrestrial planet to another. For example, of the 24 terrestrial planets that are formed in our 11 simulations, 6 planets are "dry", in the sense that they did not incorporate any embryo originally located beyond 2.5 AU. In half of the cases, the "dry" planet is the innermost one, and in the other half it was the outermost one. Curiously, in the four simulations that produced three planets, the central one is always water-rich.

(2) It may be possible that massive primitive embryos have undergone differentiation, thus losing some or most of their water. Our result for the amount of water accreted by the Earth from these embryos is then an upper limit, though a generous one (see point (4), below). We cannot give a definite answer to the differentiation problem. A reliable model for the differentiation of water-rich embryos does not exist, to our knowledge. We remark that in the asteroid belt the most massive asteroid, Ceres, appears not to be differentiated and is carbonaceous, whereas noncarbonaceous Vesta is differentiated, despite being 3× less massive than Ceres (Hilton, 1999).

(3) We have not addressed what fraction of the water carried by a giant impactor can be retained by the Earth. Zahnle *et al.* (1988) studied in detail the equilibrium between impact erosion and impact degassing only in the framework of a Safronov-like model where the accretion occurs from a multitude of small planetesimals. The question of the retention of the volatiles carried by a giant impactor has not been adequately addressed. We hope that our results will stimulate specific research on this topic. We stress, however, that if the Earth has accreted ~10% of its mass from primitive material, it should have received ~10<sup>-2</sup> M<sub>⊕</sub> of water (assuming a 10% water enrichment of primitive embryos, as for the hydrated carbonaceous chondrites). This is more than an order of magnitude larger than our nominal estimate of the mass of the water effectively accreted by the Earth. Therefore, this model allows for either a very wet Earth,

provided retention efficiencies during accretion were high, or for a minimum retention rate during giant impacts below ~10%. We thus regard the planetary embryo source as consistent with the total inventory of Earth's water, as currently understood.

### Water from Primitive Asteroids

We now quantify the delivery of water by primitive asteroids which, in the same scenario, were excited to high eccentricity orbits and bombarded the forming Earth. Remember that in our model the asteroids are bodies of negligible mass with respect to the embryos, and their dynamics is simulated in the usual test particle approximation. As for the embryos, we call primitive asteroids those originally formed beyond 2.5 AU, which are presumably in majority C-type and enriched in water.

The key difference with respect to the planetary embryos' case is that the simulations cannot handle a realistic number of asteroids. Therefore, we proceed as follows: In the simulations, we typically compute the evolution of a few hundred test particles, (see Fig. 1), which we consider as tracers of the statistical evolution of the real population of asteroids; we then compute their mean cumulative collision probability with the Earth and interpret it as the fraction of the original asteroids population that should have been accreted by the Earth.

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 ( $a, e, i$ )( $t, n$ ) as a function of time  $t$  for each of the  $N$  simulated asteroids ( $n = 1, \dots, N$ ), as well as the orbital elements ( $a_E, e_E, i_E$ )( $t$ ) and the mass  $M_E(t)$  of the forming Earth. The radius  $R_E(t)$  of the Earth is computed from the mass, assuming the present mean density of our planet. For every ( $a, e, i$ )( $t, n$ ) and ( $a_E, e_E, i_E, M_E, R_E$ )( $t$ ), the collision probability  $p(t, n)$  is computed averaging over all possible orbital configurations occurring during a precessional cycle of the orbits, and taking into account the Earth's gravitational focusing. This procedure has been accomplished with a numerical code implemented by Farinella and Davis (1992) and kindly provided to us. The mean cumulative collision probability of the asteroids with the Earth is then:

$$P(t) = \sum_n \int_0^t p(t, n) dt / N$$

The bottom panel of Fig. 3 shows  $P(t)$  as a function of time, for the simulation illustrated in Fig. 1; the top panel shows  $M_E(t)$ . As one sees, the collision probability with the Earth is equal to 0 until the time when Jupiter finishes accreting its envelope (here assumed to happen in ~10 Ma, but the exact duration is not crucial, and may be less), because the eccentricity excitation of the asteroids is not high enough to cross the orbit of the forming Earth. Conversely, after Jupiter has accreted the gas,  $P(t)$  increases rapidly, because of the enhanced orbital excitation; after 35 Ma,  $P(t)$  starts to saturate, because the vast majority of the asteroids have been dynamically eliminated (either through ejection by Jupiter or collision with the Sun). After 55 Ma, all the simulated asteroids initially beyond 2.5 AU have been eliminated.

The final cumulative collision probability is  $1.3 \times 10^{-3}$ , this means that of the total mass carried by the asteroids, only this fraction is accreted by the Earth. As a consequence, assuming that water accounts for 10% of the total asteroid's mass and that the accretion is 100% efficient, at least ~4 M<sub>⊕</sub> of asteroid material would be required beyond 2.5 AU in order to supply to the Earth its current amount of water. This is comparable to the most optimistic

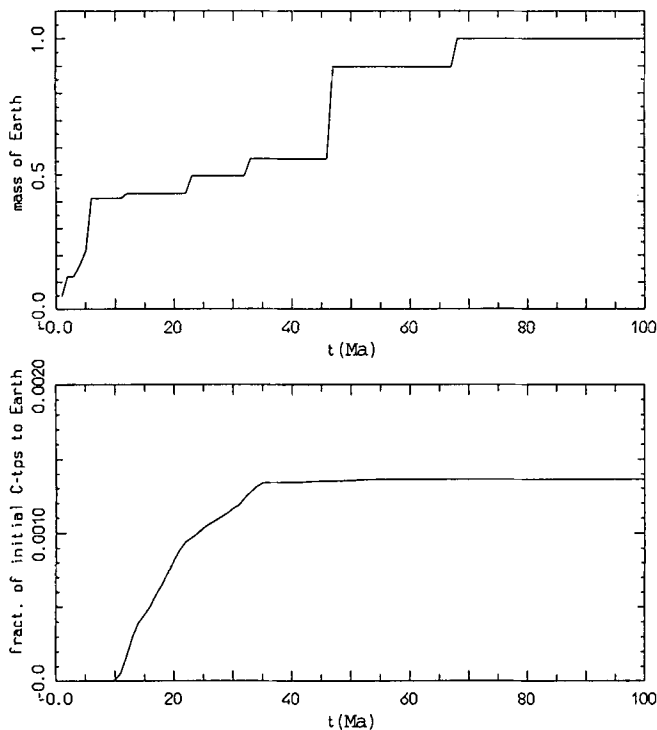


FIG 3. Top: The mass of the Earth as a function of time in the simulation shown in Fig. 1. The mass is normalized to the final mass. Bottom: The cumulative mean collision probability with the forming Earth (the  $P(t)$  defined in the text) for the asteroids initially beyond 2.5 AU in the same simulation. Notice that the cumulative collision probability saturates at a time when the "Earth" has not yet accreted 60% of its final mass.

estimates of the primordial mass of the asteroid belt. However, most of the water supplied by the asteroids is delivered between 10 and 35 Ma, when the Earth is only about half of its current mass; it is questionable which fraction of this water could have been retained by the Earth, given that several giant collisions had to occur afterwards in order to complete the planet's formation (see Fig. 3, top panel). We have done the same collision probability computation on different simulations, in order to check the variability of the result. In all cases, the final cumulative collision probability with the Earth is between  $10^{-4}$  and  $10^{-3}$ . Moreover, in most of the cases, the mass of the Earth after 35 Ma does not exceed 60% of its final mass.

It may sound puzzling that the results for the asteroids are so different from those for the embryos, presented in Water from Primitive Planetary Embryos, despite their reliance on the same simulations. To check that the different delivery efficiency of embryos and asteroids is not an artifact of the different computational methods that we have used, we have applied the same approach used for the asteroids to estimate the amount of primitive mass that should have been accreted by the Earth from planetary embryos, in the first three simulations of Table 2. The results were in agreement with those reported in Table 2. This shows that the different delivery efficiency of embryos and asteroids must rely on their statistically different dynamical evolution. In fact, the dynamics of massive bodies is very different from the dynamics of small particles. A phenomenon like dynamical friction, for instance, occurs only in the dynamics of the embryos, and not in the dynamics of the asteroids. In our simulations we observe that the embryos originally in the outer belt migrate towards the inner solar system

and reach low-eccentricity orbits in the terrestrial region more easily than massless asteroids. As a consequence, their collision probability with the forming terrestrial planets is highly enhanced.

#### DELIVERY OF WATER DURING THE DEPLETION OF THE PRIMORDIAL ASTEROID BELT: ALTERNATIVE MODELS

Alternative models have been proposed to explain the primordial depletion and excitation of the asteroid belt, which do not invoke the presence of massive embryos. Here we estimate what these embryo-free models would imply for the water budget of the Earth.

As is well known, the perihelion secular resonances (resonances between the precession frequencies of the perihelia of an asteroid and of a planet) force a slow increase in the eccentricities of the resonant asteroids. Ward *et al.* (1976) first proposed the idea that secular resonances could have swept the asteroid belt as a result of the dissipation of the primordial nebula. Later, Gomes (1997) showed that a radial migration of a few tenths of an AU of Jupiter and Saturn could have produced a similar effect. If the location of secular resonances moves through the belt in  $\sim 1$  Ma, most of the asteroids stay in a resonant state for a time that is sufficiently long to acquire planet-crossing eccentricities. This results in a substantial mass depletion of the asteroid belt. According to Lecar and Franklin (1997), the secular resonances sweep the belt in  $\sim 1$  Ma if the nebula has a surface density

$$\sigma = \frac{\sigma_0}{r^{1.5}} \exp^{-t/\tau} \quad (3)$$

where  $t$  is the time,  $r$  is the heliocentric distance in AU,  $\tau = 240\,000$  years, and  $\sigma_0 \approx 1500$  g/cm<sup>2</sup>; in this case, 99% of the asteroids become either Jupiter- or Mars-crossing (Franklin and Lecar, 2000).

In the classical model of secular resonance sweeping the asteroids' semimajor axes are preserved. Morbidelli and Gladman (1998) computed that for the asteroids that become Earth-crossing at 2.5 AU, the cumulative collision probability with our planet is  $\sim 10^{-3}$ . The collision probability drops very rapidly with the semimajor axis, being  $\sim 10^{-4}$  for the asteroids at 2.8 AU and  $\sim 10^{-6}$  for the asteroids at 3.3 AU. With such low collision probabilities, the asteroids originally beyond 2.5 AU could not carry enough water to the Earth, unless their initial cumulative mass is at least  $10 M_{\oplus}$ , which is unlikely. Therefore, we can conclude that in the classical secular resonance sweeping model the bulk of Earth's water cannot come from the asteroid belt.

Franklin and Lecar (2000) have developed a new model where in addition to the secular resonance sweeping they take into account the effects of gas-drag. They have shown that asteroids smaller than  $\sim 20$  km in radius, once their eccentricity is pumped above 0.2–0.3, can spiral into the inner solar system under the effect of gas drag, by rapidly decreasing their semimajor axes. In the case with  $\tau = 240\,000$  years, Franklin and Lecar found that 97.8% of the outer belt asteroids with radius between 5 and 10 km have a final semimajor axis smaller than 2 AU. The effect is much less pronounced for bodies smaller than 5 km, and decays in importance also for bodies larger than 10 km. If the radius is in the range 10–20 km, 71% of the outer belt asteroids decay to  $a < 2$  AU, and this fraction drops to 18.5% for bodies between 20 and 50 km and to 1% for bodies larger than 50 km.

Once in the inner solar system, the collision probability of the drag-delivered bodies is highly enhanced. For instance, starting from a population of asteroids initially between 1 and 2 AU in the framework of the Earth accretion model discussed in The Delivery of Water During the Depletion of the Primordial Asteroid Belt, we

obtain a mean cumulative collision probability with the forming Earth of  $5 \times 10^{-2}$ . With this high collision probability, Franklin and Lecar's result implies that  $0.1 M_{\oplus}$  of small carbonaceous asteroids would suffice to deliver the lower limit amount of water presently on Earth, if we assume a 10% water enrichment of the asteroids and a 100% delivery efficiency during the impact. These assumptions are evidently very optimistic, but on the other hand it is plausible that more than  $0.1 M_{\oplus}$  originally existed in the outer asteroid belt in the form of asteroids between 5 and 20 km in radius.

Although this seems to be a possible scenario for the origin of water in a relatively dry Earth, we argue that some caution is needed for several reasons. First, the transport of the small carbonaceous asteroids into the inner solar system could happen only after Jupiter was formed but before the nebula was completely dissipated. It is questionable whether the lapse of time between these two events could be long enough. Of more concern is that bodies moved inward by nebular gas drag would arrive in the inner solar system in a very early epoch, when the Earth is still quite small. Then, according to our terrestrial growth computation, 70% of the bodies that ever collide with the Earth do so when the latter is less than 60% of its current mass. Retention during the impact process would have been smaller than at later times; moreover the giant impacts subsequently could have removed much of the early accreted water. Finally, according to Nagasawa *et al.* (2000), Franklin and Lecar's scenario is not realistic for describing the primordial sculpting of the asteroid belt, because it fails to reproduce the excitation of the inclinations of the surviving asteroids.

Nagasawa *et al.* (2000) proposed an alternative model to explain the mass depletion of the asteroid belt and the excitation of both eccentricities and inclinations. Their model requires that the nebula is dissipated by an outward migration of its inner edge, so that the secular resonance sweeping occurs after all the gas has left the asteroid belt. No migration by gas drag of primitive asteroids into the inner solar system can occur in this model. Franklin and Lecar (pers. comm.), on the basis of an analytic study by Lemaître and Debru (1991), respond that a nebular surface density  $\sigma = (\sigma_0/r) \exp(-t/\tau)$  would give a similar result to that obtained with Eq. (3) with respect to eccentricity excitation and inward migration of small asteroids, and in addition also account for the excitation of the asteroids' inclinations. However, quantitative numerical simulations have not yet been done to our knowledge.

The transport of small asteroids from the outer belt to the inner solar system by gas drag also could have been a relevant phenomenon in the context of the model of scattering embryos, discussed in Delivery of Water During the Depletion of Primordial Asteroid Belt. In fact, in the simulation shown in Fig. 1, almost all the asteroids originally in the outer belt have acquired, at least temporarily, an eccentricity larger than 0.3 by the time that Jupiter is formed (within 10 Ma). Because gas drag becomes effective at reducing the semi-major axis when the eccentricity exceeds 0.2–0.3 (Franklin and Lecar, 2000), a large number of small primitive asteroids may have reached the environment of the forming Earth during the first 10 Ma. Unfortunately, the effect of gas drag is not yet included in our *N*-body integrator, so that we cannot as yet quantitatively check this hypothesis.

Note that, despite their differences, all models imply that the primordial depletion of the asteroid belt occurred very early, during the dissipation phase of the nebula, or shortly after. This is in agreement with the observation that the fragile basaltic crust of the asteroid Vesta survived almost intact (Davis *et al.*, 1994). But this

then implies that the phase of high production of dust in the asteroid belt could not have lasted for several  $10^8$  years, as conversely required by models in which asteroidal interplanetary dust particles deliver the Earth's inventory of water (Pavlov *et al.*, 1999).

### THE COMETARY CONTRIBUTION

The delivery of water from the outer planetary regions is easier to estimate than the delivery from the asteroid belt. The difference is that the asteroid belt is stable in the framework of the present-day solar system, so that we need to rely on scenarios of primordial evolution to understand how the bodies left the belt and came to interact with the Earth. Conversely, most of the bodies initially among the giant planets have unstable orbits (Holman and Wisdom, 1993). To estimate the order of magnitude of the Earth collision probability of primordial comet-sized planetesimals beyond 4.5 AU, it is therefore sufficient to study the dynamical evolution of test particles in the present planetary configuration. We are of course aware that the primordial solar system was different from the present solar system, but on the other hand the dynamics of comets is so strongly dominated by the scattering action of Jupiter and Saturn that it is probably insensitive to small variations in the position of the latter as well as to the possible presence of other planetary embryos. An additional advantage is that the cometary contribution that we estimate in this section should be correct independently of which model, among those described before, is adequate for describing the primordial sculpting of the asteroid belt.

Below, we separate the discussion on the comets initially in the Jupiter–Saturn region from that on the comets initially in the Uranus–Neptune and trans-Neptunian region. In fact, the comets from these two primordial reservoirs should have undergone different dynamical evolutions, and should have carried water with different D/H ratios. The comets originally between Saturn and Uranus can be considered as an intermediate group, from both the dynamical and chemical viewpoints.

#### Water from the Jupiter–Saturn Region Comets

For our numerical experiment, we consider test particles with semimajor axes ranging from 4.5 to 9 AU with nonregular spacing. The *a*-spacing is 0.002 AU between 4.5 and 5 AU (250 particles), 0.0004 AU between 5 and 7 AU (5000 particles), and 0.0025 AU between 7 and 9 AU (800 particles). The reason for this choice is to have enough statistics in the region 5–7 AU that has been conjectured by Delsemme (1999), on the basis of an analytic Safronov-like model, to be that characterized by maximal efficiency of the delivery of material to the Earth. For all test particles, the values of the angles are chosen randomly, whereas the eccentricities and inclinations are set equal to zero. A natural objection to this setup is that the comets could not have circular orbits, having been already dynamically excited during the growth of the giant planets' embryos. However, Petit *et al.* (1999) already tested the effect of the growth of Jupiter on a population of massless planetesimals and found that this transition phase is essentially unimportant for the transport of material to Earth-crossing orbits.

Each test particle was followed using the swift-rmv3 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 the Earth (assumed to be on its present orbit) is computed over the test particle's lifetime with the method discussed in Water from Primitive Asteroids.



The resulting collision probability, averaged over 0.5 AU bins, is shown in the histogram of Fig. 4 to be on the order of  $(1-3) \times 10^{-6}$  per particle in the 5–8 AU region, decreasing to  $5 \times 10^{-7}$  for larger semimajor axes.

The lifetime of the bodies in the Jupiter–Saturn zone is extremely short. Excluding the bodies in stable Trojan-like orbits, we find a median lifetime of  $1.5 \times 10^5$  years, whereas  $<10\%$  of the integrated bodies have not yet been dynamically eliminated in 2 Ma. This also implies that the phase of high production of dust by the primordial comets should have been very limited in time and thus is an additional argument against a significant role of cometary interplanetary dust particles in the delivery of water to the Earth (Pavlov *et al.*, 1999).

At the time of formation of the giant planets, there must have been in the outer solar system many tens of Earth masses of icy planetesimals. Pollack *et al.* (1996) showed that to build the planetary cores within the dissipation time of the nebula ( $\sim 10$  Ma),  $100 M_{\oplus}$  of solid material (rock and ices) had to exist in the 5–30 AU region. This estimate is supported by Guillot and Gladman (2000), who showed that the comets of Pollack *et al.* (1996) would also account for the amount of heavy elements in the gaseous envelopes of the giant planets (Guillot, 1999), provided the latter passed through a phase of approximately 1–10 Ma during which they had greatly increased cross-sections, relative to today, for the capture of planetesimals. An independent estimate of 50–200  $M_{\oplus}$  for the mass of the comets disk has been obtained by Hahn and Malhotra (1999) to account for the formation of a substantial Oort Cloud.

A surface density of solid materials that decays as  $1/r^2$  implies that  $\sim 40\%$  of the planetesimals are in the Jupiter–Saturn region. But a local enhancement of icy material may have existed around 4–5 AU if a snowline existed in that region (Morfill and Volk, 1984). Water vapor inward of the snowline was transported outward by diffusion (Cyr *et al.*, 1998) or advection (Stepinski and Valageas, 1997) so that much of it could have encountered such a snowline and

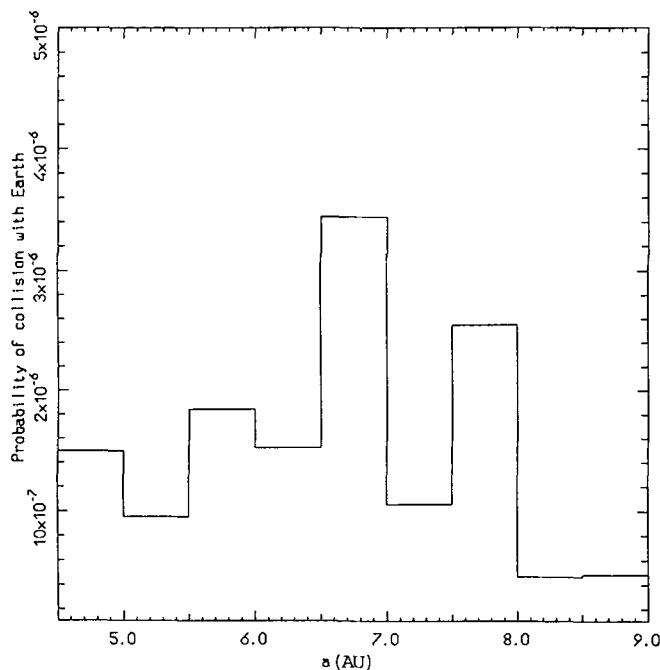


FIG. 4. Mean Earth collision probability of comets initially in the Jupiter–Saturn region, binned with respect to the initial semimajor axis.

condensed out (Morfill and Volk, 1984). It is therefore possible that such a snowline could have acted as a cold-finger for the removal of water vapor, enriching the 4–5 AU region with water ice derived from portions of the nebula well inward of that radial distance. A simple model of such a snowline suggests that up to  $20-30 M_{\oplus}$  of water ice could have been present within 4–5 AU just attributable to the cold-finger effect of water vapor trapping. A more elaborate model incorporating details of the nebular transport might yield different values, but the key point—that such a cold finger enriches the amount of mass available in the 4–5 AU region—would remain valid.

For all these reasons, we consider reasonable that about 50–100  $M_{\oplus}$  of comets existed in the Jupiter–Saturn region. These comets should be characterized by a low D/H ratio on the order of 4–6 in units of the protosolar value, according to recent models of the solar nebula which compute exchange of D and H between gaseous and condensed phases (Drouart *et al.*, 1999; see also Lunine *et al.*, 2000).

With the mean Earth-collision probability shown in Fig. 4, we thus obtain that  $\sim 10^{-4} M_{\oplus}$  should have been delivered to the Earth. Even assuming that these comets are mostly made of ice, the amount of water accreted by the Earth would be only a fraction (2–20%) of the total amount of water presently existing on Earth. We regard this number as an upper limit: because of the short dynamical lifetime of the comets, their infall on the Earth should have occurred in the first million year after Jupiter's formation, when the Earth was presumably a smaller target on a more eccentric orbit than the present planet. This would have reduced the collision probability with respect to that reported in Fig. 4 and led to both a low efficiency of retention of water during the impact and a high probability of loss during subsequent giant impacts. Moreover, if Jupiter and Saturn had enhanced cross-sections during a considerably longer phase, the fraction of the comets population scattered onto Earth-crossing orbit should have been much smaller than in our simulation, so that the results reported in Fig. 4 would overestimate their Earth collision probability. In summary, we disagree with Delsemme's (1999) conclusion that comets from the Jupiter zone could account for the delivery of the bulk of Earth's water.

The reasons for the difference between our and Delsemme's results (1999) are multiple. Our result is based on a large number of direct numerical integrations. Conversely, Delsemme's estimates are based on computations by Safronov (1972) and by Ip and Fernández (1988). The former used an analytic formalism, in which the dynamics is totally dominated by close encounters; resonances and dynamical barriers to diffusion, attributable to the presence of large planets, are not present in the model. Ip and Fernández used the more sophisticated Öpik's (1976) theory of close encounters; in this case, the dynamical barriers to diffusion are present, but both secular and mean motion resonances are not taken into account as well as possible correlations between subsequent encounters. The lifetimes of small bodies obtained with Öpik's theory are typically an overestimate of those obtained by direct numerical integrations, as recently shown by Dones *et al.* (1999). All these factors make Delsemme overestimate the cometary contribution with respect to our work.

#### Water from the Trans-Uranian Region Comets

From the above considerations on the total mass of the disk, we estimate that about  $20-30 M_{\oplus}$  of comets primordially existed in the Uranus–Neptune region. In addition, one should consider that  $\sim 30 M_{\oplus}$  are missing from the Kuiper Belt (Stern, 1996; Weissman and Levison, 1997). If this missing mass was lost by collisional grinding (Stern and Colwell, 1997), most of it should have never

entered the inner solar system; conversely, if the mass loss of the Kuiper Belt occurred because most of the bodies were emplaced in Neptune crossing orbits due to some primordial excitation mechanism (Petit *et al.*, 1999), the missing mass of the Kuiper Belt should be added to the cumulative mass of trans-Uranian cometesimals that are potentially capable of reaching the Earth.

From the D/H measurements in long-period comets cited in the Introduction, and the quoted models by Drouart *et al.* (1999) and Lunine *et al.* (2000), it is reasonable to expect that the cometesimals in the trans-Uranian region were made of water with a D/H ratio of  $\sim 12$  (in units of the protosolar value).

The dynamical lifetime of trans-Uranian cometesimals is much longer than that of the bodies in the Jupiter–Saturn region. According to Holman and Wisdom (1993), most of the bodies in the Uranus–Neptune region take  $10^6$ – $10^7$  years to intersect the orbit of a planet, after which they evolve as Centaurs and are consequently dynamically eliminated on a timescale of several million years (Dones, 1996). Beyond Neptune the half-life of the bodies, after their first encounter with the planet, is  $\sim 10^8$  years (Duncan and Levison, 1997).

The mean collision probability with the Earth of the comets in the Neptune region has been recently estimated to be  $\sim 10^{-6}$ , by Levison *et al.* (2000). Note that this number is close to the mean Earth collision probability illustrated in Fig. 4, suggesting that this value should be typical of the entire giant planets region. We therefore expect that  $\sim 5 \times 10^{-5} M_{\oplus}$  of cometary material from the trans-Uranian region could have been delivered to the Earth. Even assuming a 100% water composition of this material and a 100% impact efficiency, this would imply the delivery of  $\sim 10\%$  of the water presently existing on our planet. This result, that comets are a minor source of Earth's water, is consistent with the observation that the D/H ratio of Earth's water is half of that expected for trans-Uranian comets.

#### COMPARISON WITH GEOCHEMICAL DATA

In our dynamical model, the amount of high D/H water of cometary origin on Earth does not exceed on the order of 10% of the total budget. As a consequence, the original D/H ratio of Earth's water was only slightly elevated and remained very similar to the chondritic values. An upper bound on the cometary contribution also can be derived *via* an isotopic H mass balance between carbonaceous chondrites, comets, and the present-day Earth (Deloule *et al.*, 1998), namely:

$$F_C \leq (149 - 128) / (309 - 128) \leq 0.12$$

where  $F_C$  is the fraction of water carried by high D/H comets, 149 is the present-day Earth D/H ratio, 309 is the value for cometary water, and 128 (all units are  $\times 10^{-6}$ ) is the minimum possible D/H ratio for the primitive Earth, corresponding to the minimum value measured in carbonaceous chondrites (see Volatile Elements Inventory). Hence, the D/H ratio of the present-day Earth's water argues for a cometary contribution not exceeding 12%, in good agreement with our accretion model.

Our model also allows us to understand why the D/H ratio in the primitive mantle was somewhat smaller than the average value for carbonaceous chondrites (see Volatile Elements Inventory). In fact, the one or a few embryos from the outer asteroid belt that should have delivered most of the water to the Earth presumably had D/H ratios in the range of the values found in carbonaceous chondrites, but there is no reason to expect that they had D/H ratios exactly equal to the average chondritic value.

Conversely, a paradox is evident when we compare the terrestrial rare gas budget with respect to the typical carbonaceous chondritic abundances. We define the following depletion factor of the Earth's atmosphere compared to carbonaceous chondritic abundances:

$$E(RG) = \frac{[RG]_{Atm} / [H_2O]_{Atm}}{[RG]_{CC} / [H_2O]_{CC}}$$

where  $RG$  stands for Ne or Xe,  $[.]_{Atm}$  denotes the concentration in the atmosphere, and  $[.]_{CC}$  denotes the concentration in the carbonaceous chondrites. Using the values reported in Table 1, we obtain  $E(\text{Ne}) \approx 8$ – $10$ , whereas  $E(\text{Xe}) \approx 1$ . The Earth therefore presents an excess of Ne with respect to what would be expected in a scenario where all the rare gases and the water have been delivered by carbonaceous chondritic material.

We briefly speculate about a possible way out of the paradox that would be compatible with our scenario. It consists of diluting the Ne and Xe of chondritic origin with Ne and Xe of solar nebula origin, captured, and outgassed by the proto-Earth. More precisely, the Earth should have accreted Ne and Xe in solar proportion ( $\text{Ne/Xe} = 7 \times 10^5$ , *i.e.*,  $\sim 1500\times$  the chondritic value) during the early phase when the protoplanet was still embedded in the solar nebula, because of the existence of a magmatic ocean, which has been argued to be plausible on several grounds (see, for instance, Abe *et al.*, 2000). Subsequently, the primitive Earth's atmosphere could have fractionated the rare gases during an epoch of atmospheric escape (Zahnle *et al.*, 1990; Pepin, 1991). The initially very high Ne/Xe ratio was reduced but plausibly remained larger than  $10\times$  the chondritic ratio, and the leftover atmospheric Ne and Xe were heavily isotopically fractionated (see the detailed calculations in Tolstikin and Marty, 1998). Subsequently, the Earth should have accreted water and rare gases from a few carbonaceous chondritic embryos, in chondritic proportion. In this scenario, it is then possible that the Ne in the present-day atmosphere is predominantly of solar origin, the Xe is a mixture of solar and chondritic components, and the water is dominantly chondritic. This would be compatible with the values of  $E(\text{Ne})$  and  $E(\text{Xe})$  and with the observed isotopic fractionation of both atmospheric Ne and Xe.

The physics and chemistry involved in this scenario are very complex. A deeper study would be required to properly examine this scenario. Here, we simply show that our model on the delivery of water with carbonaceous chondritic material should not be ruled out *a priori* because of the rare gases.

#### CONCLUSIONS

This paper has been motivated by new geochemical and astronomical observations that have shown the inconsistency of a cometary late veneer scenario for the origin of water on Earth.

For the most plausible reservoirs of water in the primordial solar system—the asteroid belt and the giant planets region—we have studied the characteristic delivery efficiencies to the forming Earth and the corresponding timescales. In the absence of a widely accepted model for the primordial depletion of the asteroid belt, we have analyzed several competing scenarios. We have found that the sole explanation for the delivery of a sufficiently large amount of water with low D/H ratio relies on the existence of massive planetary embryos in the asteroid belt. This model, first proposed by Wetherill in 1992, gives satisfactory results for what concerns the accretion of the terrestrial planets (Chambers and Wetherill, 1998) and the primordial sculpting of the asteroid belt (Petit *et al.*, unpubl. data, 2000). The results of this paper further strengthen its validity.

We caution, however, that none of the existing models on terrestrial planets formation and solar system primordial evolution is optimal.

According to our current best understanding of solar system formation and putting together the results of the computations presented in this paper, we find that the Earth has accreted water throughout its formation. We summarize here the different phases of accretion, in chronological order.

The Earth formed on a timescale of  $10^8$  years by the high velocity collisions of planetary embryos (Chambers and Wetherill, 1998; Agnor *et al.*, 1999). At the beginning of its growth, the Earth accreted only embryos originally formed in the Earth region, which should have been water-depleted both in standard nebular models, and (especially) in models in which condensation of water at 4–5 AU depletes the inner nebula of water vapor.

However, while the Earth's embryo was still embedded in the solar nebula (<10 Ma), hydrated 10 km asteroids came from the outer belt transported by gas drag. The amount of water that could have been accreted from these asteroids by the forming Earth is very model dependent, and, potentially, could have been comparable to the amount of water presently existing on our planet. However, because of the small mass of the Earth at that time, very little of it should have been retained during the numerous giant collisions that subsequently completed the Earth's accretion.

Shortly after that Jupiter accreted its envelope and reached its current mass (within ~10 Ma), the forming Earth experienced a shower of asteroids and comets attributable to the rapid depletion of the asteroid belt and of the Jupiter region. However, this shower lasted only for a few times  $10^6$ – $10^7$  years and delivered to the Earth only a minor fraction of the present amount of water. The Earth being still small at that time (presumably less than half its present mass), most of the accreted water was subsequently lost.

Towards the end of its formation (several  $10^7$  years), the Earth began to accrete planetary embryos originally formed in more distant regions. Our simulations show that it is very likely that in this process the Earth also accreted a few embryos coming from the outer asteroid belt, which were heavily hydrated on the basis of meteorite analyses and modeling of the solar nebula. This could have brought to the Earth ~10× the present amount of water in the crust, and in principle satisfied even the extreme "wet Earth" model favored by some geochemists. What fraction of this water could have survived up to the present time is an open question; however, the Earth being near the end of its accretion, we argue that this corresponds in fact to the bulk of the water that is presently on our planet.

Finally, once its formation was completed, the Earth was bombarded by comets coming from the trans-Uranian region, and in particular from the Kuiper Belt. This was a late veneer phase, possibly coinciding with the late heavy bombardment: the only period of the Earth's history during which a significant amount of water with high D/H ratio was delivered. However, at most only ~10% of the present amount of water could have been captured in this way.

As discussed in Comparison with Geochemical Data, this scenario of accretion of the water, dominated by the carbonaceous chondritic contribution, is compatible with the measured value of the D/H ratio of Earth. A paradox, conversely, is raised by the noble gas budget of our planet, which does not resemble carbonaceous-chondrites. In the same section, we have speculated on a possible way out of the paradox, where the noble gases delivered with the water are mixed with those that, captured from the solar nebula,

survived an intense phase of hydrodynamic escape. The chemistry involved is highly complicated, and this speculation will need to be investigated more deeply.

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