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Cometary Origin of the Biosphere

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Most of the biosphere was brought on the primitive Earth by an intense bombardment of comets. This included the atmosphere, the seawater and those volatile carbon compounds needed for the emergence of life. Comets were thrown into the inner Solar System by the strong perturbation induced by the growth of the giant planets' cores. The bulk of the Earth's bombardment came from those comets that accreted in Jupiter's zone, where the original deuterium enrichment had been diminished by steam coming from the hot, inner parts of the Solar System. This steam had condensed into icy chunks before their accretion into larger cometary nuclei. In contrast, comets that accreted in the zones of the outer giant planets kept their interstellar isotopic enrichments. Those comets contributed to the Earth's bombardment for a small amount only; they were mostly ejected into the Oort cloud and are the major source of the long-period comets observed today. The short-period comets, which come from the Kuiper Belt, should also have the same interstellar enrichment. The deuterium enrichment of seawater, accurately predicted by the previous scenario, has become one of the best telltales for the cometary origin of our biosphere. This cometary origin may have far-reaching cosmological consequences, in particular for the origin of life in other planetary systems. © 2000 Academic Press

INTRODUCTION

My "Recollections" (Delsemme 1998a) summarized my early efforts covering a time span of more than 40 years to unravel cometary chemistry. I do not want to repeat myself. For this reason, this review will tell the story of a more recent and more controversial endeavor that convinced me that the bulk of the biosphere has been brought onto the primitive Earth by a very large bombardment of comets.

We all know that the biosphere is that part of the Earth's crust, waters, and atmosphere where living organisms can survive. Since life emerged very early on the primitive Earth, the origin of the biosphere may be intricately linked to the emergence of life. The historical development of the ideas about the origins of life is much too long to be discussed here. Suffice it to say that comets have been linked early to life's origin, because cometary spectra showed the presence of CN, C_2, C_3, CH, CO, etc. These fragments of organic molecules in the coma suggested the possible presence in the nucleus of *prebiotic molecules*, that is, of molecules ready to get life started if other prerequisite conditions were met. Among the precursors of these ideas are Chamberlin and Chamberlin (1908) and Oparin (1936); Lederberg and Cowie (1958) and Oró (1961) came later.

From my "Recollections" (Delsemme 1998a) it is apparent that I was very slow and reluctant to accept that the biosphere could be attributed to an early bombardment of comets. I wanted first to understand the nature and the chemical origin of the molecular fragments, ions, and radicals observed in the heads and tails of comets. I waited for 25 years (from 1950 to 1975) before daring to speculate on the connection between comets and interstellar molecules (Delsemme 1975). I then concluded with surprise that many prebiotic molecules, such as purines, pyrimidines, and amino acids, might already be present in comets. However, at first I could not believe that they could survive the intense heat produced by the cometary impact on Earth.

I found a possible explanation the following year (Delsemme 1976). Those prebiotic molecules that survive onto the Earth use an indirect route. They are ejected first in the dust grains present in those tails so conspicuously displayed by most comets that enter the inner Solar System. This dust does not escape entirely; it is stored in an interplanetary cloud surrounding the Sun, which is the source of the zodiacal light. This cloud of dust extends beyond the Earth; it explains the origin of the dust particles that enter our exosphere and are gently braked in the upper atmosphere, falling slowly without much heating (Delsemme 1976). They indeed contain prebiotic molecules that will reach the ground unharmed, as demonstrated later by their chemical analysis (Brownlee 1985) after their capture by the U2 aircraft of NASA. We will see later why, during the early comet bombardment, this interplanetary cloud of dust was at least 100,000 times as dense as now and remained a very important source of prebiotic molecules for the first billion years of the early Earth.

Later, Chyba and Sagan (1996) emphasized that very large impacts, by exploding into the atmosphere, can also release fragments with unheated interiors. Pierazzo and Chyba (1999) have confirmed that delivery of amino acids by large impacts is possible. I still think that the interplanetary dust process was much

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TABLE I
Relative Elemental Abundances in Life, in Comets, and in the Frost of Space[c]

Element	Bacteria %	Mammals %	Interstellar frost %	Volatile fraction of comets %
Hydrogen	63.1	61.0	55	56
Oxygen	29.0	26.0	30	31
Carbon	6.4	10.5	13	10
Nitrogen	1.4	2.4	1	2.7
Sulphur	0.06	0.13	0.8	0.3
Phosphorous	0.12	0.13	—	(0.08)[a]
Calcium	—[b]	0.23	—	—

[a] Phosphorus has not been observed in comets; (0.08) is its cosmic abundance, which is reasonably expected to be in cometary snows.

[b] Calcium is not present in primitive bacteria; its use in shells and skeletons is a recent discovery of evolved animals.

[c] This comparison (Delsemme 1978) was done only to see whether there was any possible connection between life and cosmic data.

more effective than large impacts to deliver prebiotic molecules to Earth, but the point is that there is no more any reason to doubt that the delivery to Earth of unharmed prebiotic molecules is possible, in contradiction to what some biochemists still believe.

CONTROVERSY WITH FRED HOYLE

At the 1977 Welch Conference on Cosmochemistry, in Houston, Texas, I mentioned the surprising similarity of the relative elemental abundances in comets and in living organisms (Delsemme 1978). This comparison is repeated in Table I. That very day, Fred Hoyle accompanied me to my hotel room and tried to convince me that the reason for this similarity was that bacteria preexisted already in comets. I have told in detail, in the popular book “Our Cosmic Origins” (Delsemme 1998b), the story of my six-year controversy with Fred Hoyle. Because of this contention, I decided in 1977 that it was time for me to learn more about the origin of life. I am still grateful to Fred Hoyle, who was instrumental in this decision.

This motivated my attendance at the 6th ISSOL Conference in Jerusalem, in June 1980. This is when I met John Oró for the first time and learned that, as a biochemist who had studied the polymerization of HCN, he had already connected comets with the origins of life. At that time, I also heard of a misconception prevailing among some biochemists who believed that HCN (and not only the radical CN) had been discovered in Comet Halley during its 1910 passage. This mistake is repeated in Deamer and Fleischacker (1994). HCN has been identified in comets by radioastronomy more than half a century after CN.

THE ORIGIN OF LIFE

My Jerusalem paper (Delsemme 1981a) discussed the nature and the origin of the organic molecules in comets and called the fact that prebiotic organic molecules might have been brought unharmed to Earth by comets, from interstellar space through solar nebula processes, “an intriguing possibility.”

In October 1980, Cyril Ponnamperuma invited me to a colloquium entitled “Comets and the Origin of Life,” organized in College Park, Maryland (Ponnamperuma 1981). Although only one third of the participants directly addressed the connection suggested by the title, there was a consensus that marked a turning point in the acceptance of this idea. My paper (Delsemme 1981b) discussed with care all the possible locations where life could have emerged and concluded that the early Earth was the most likely place, because it had not only liquid water, but also the proper oxidation-reduction ratio, without free oxygen but with some free hydrogen that diminished slowly with time; hence the future biosphere went through the optimal conditions for the emergence of life. Comets had the right chemistry to get the whole process started, but this process cannot go through alternate cycles of polycondensation without using liquid water. In Delsemme (1982), I showed that the production of liquid water, by the heating of cometary cores with radioactive Al 26, had no empirical support. It happens that Mg 26, the by-product of the radioactive decay of Al 26, has not been detected in *C*1 chondrites. These volatile-rich chondrites come from the outer fringe of the asteroid belt and are in many respects similar to the comets that were formed in Jupiter’s zone.

In July 1983, I attended the 7th International Conference on the Origins of Life in Mainz, Germany, where I suggested for the first time that the whole biosphere could have been created by an intense early bombardment of the primitive Earth by comets. During the first billion years, the immense amount of cometary dust collected by the interplanetary cloud steadily fed the upper atmosphere of the Earth with prebiotic molecules. Such a scenario explains the otherwise surprising coincidence that life emerged as soon as the conditions were no more hostile to its survival (Delsemme 1984). However, I had become aware that the matter could not be clarified by theory only, but needed empirical facts related to the formation of the planets. In particular, I wanted to clarify: (a) the origin of the Earth’s volatiles, and (b) the possible role of comets in the Earth’s volatile inventory.

PLANET FORMATION

For this purpose, let us go back to the time before the formation of the planets. We know that the nature of primitive meteorites supports the existence of a dust sedimentation from the nebular gas. Dust sedimented to the mid-plane of the planetary nebula, where it formed large rings at the distances of the future planets. We will consider the case of the giant planets later, and we discuss first the formation of the Earth. In the rings, the grains’ temperature not only depended on the heliocentric distance, but also continuously varied with time. Cameron (1978) illustrates this feature (see Fig. 1).

During the accretion of the nebular gas, the temperature rises steadily. It reaches a maximum when accretion stops and then it diminishes during mass loss. When the accretion subsides and

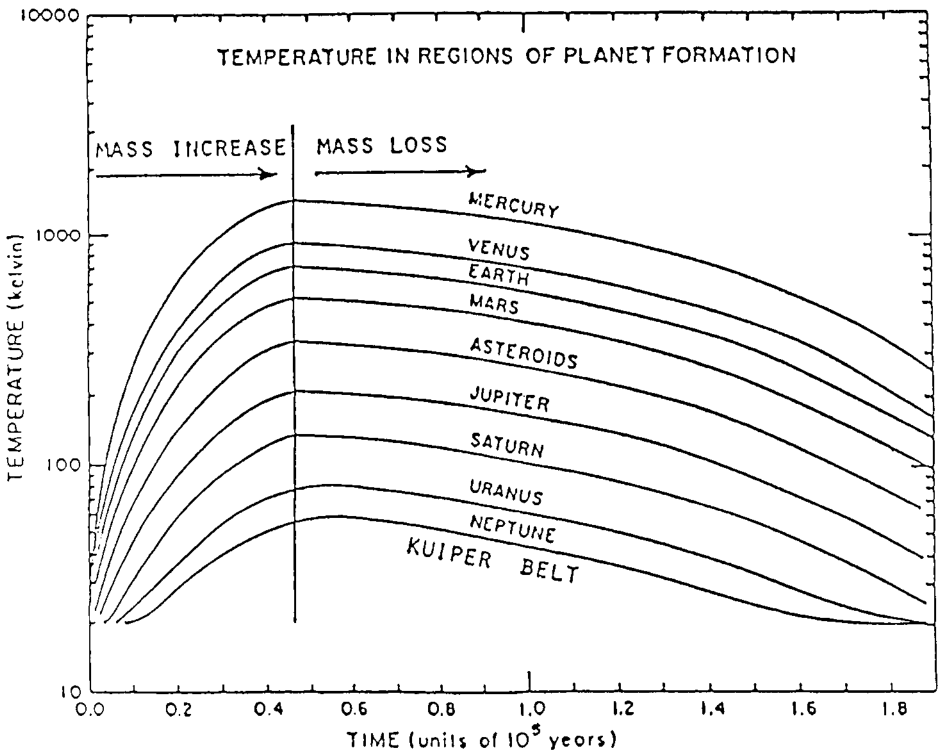

FIG. 1. Temperature evolution of the accretion disk in the zones of planetary formation (from Cameron 1978). The disk temperature is maximum just before the dust sediments to the mid-plane, where grains will agglomerate into large objects. A cold front able to condense steam into snow appears first beyond Jupiter's zone and moves to the asteroid belt in some 100,000 years, explaining the origin of water in carbonaceous chondrites.

stops, dust is not supported by gas turbulence any more; hence this is the time when it sediments to the mid-plane. The maximum grain temperature comes therefore just at the time when the sedimentation is beginning and just before grain agglomeration into larger and larger chunks.

In a model such as Cameron's, the maximum temperature reached by the grains of dust at a distance of 1 AU is on the order of 700 K. This would already be enough to degas the dust before it accretes into larger chunks. If the primitive Earth was totally degassed, water and other volatiles must have been brought later by objects with more volatile material, such as comets. Of course, we must be wary of models, because too many of their parameters are uncertain. What is the empirical evidence (Delsemme 1987)?

FORMATION OF THE EARTH

The accretion temperature of the solid grains that form an individual planet is not easy to deduce from the planet itself, because more recent heating due to its gravitation has erased early telltales of its formation temperature. Only in the asteroid belt can we find objects that are small enough not to have been heated later by their gravitation, because it remained negligible. These objects are the source of the meteorites called chondrites (ordinary chondrites from the S asteroids, and carbonaceous chondrites from the C asteroids). I deduced (Delsemme 1991) that it was possible to establish the sedimentation temperature of most of the grains that agglomerated later to form the Earth.

The original separation of the C from the S asteroids is still rather easy to see now (Morrison 1977) at a distance of 2.6 AU, because of their slow orbital diffusion. It so happens that the differential depletion of the most volatile metals found in the carbonaceous and in the ordinary chondrites (Larimer and Anders 1970, Anders 1971) points unambiguously to a maximum temperature of 450 K, at the original distance of 2.6 AU separating the two classes. This is the best yardstick known to normalize Fig. 2.

In order to assess the maximum temperature reached in the Earth's zone at the epoch of dust sedimentation, a temperature gradient is needed for the mid-plane of the protoplanetary disk. In the absence of an outside influence, the virial theorem implies that this gradient must be exactly -1. However, Lewis (1974) has shown that if the empirical aggregation temperatures of the different planets fit rather well with a gradient of -1, then they fit even better with a gradient of -0.9. I concluded (Delsemme 1991) that, at the epoch of Earth's accretion, in the zone from 0.8 to 1.3 AU, the grains' temperature reached a maximum varying from 800 to 1500 K. This implies that all solid grains located in this zone were silicate and reduced iron grains that had already been thoroughly degassed. All carbon was in CO, all nitrogen in gaseous N2, and all water in steam.

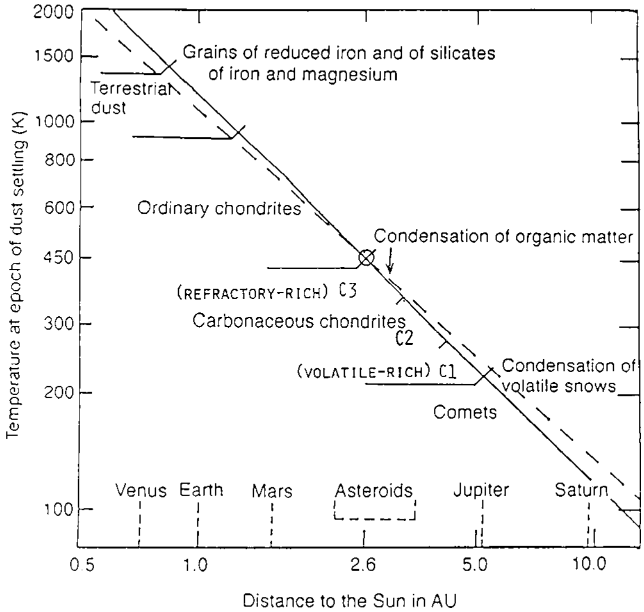

FIG. 2. Maximum temperature distribution in the mid-plane of the accretion disk, found empirically from the loss of volatile metals in chondrites. The distance of 2.6 AU separates, in the asteroid belt, the ordinary from the carbonaceous chondrites. The two possible temperature gradients, −0.9 (dotted line) and −1.0 (solid line), are not very different. The cold front that condenses steam will move from Jupiter's zone to the asteroids'. The three types of carbonaceous chondrites have been located according to their content of volatile elements.

The accretion temperature of the protoearth was too hot to retain any volatiles.

RADIAL MIXING

In the later stages of planet agglomeration, radial mixing extended further and further (Wetherill 1980, 1990). When the radii of the largest bodies reached the range of 4000 to 5000 km, the radial mixing had spread to a much wider zone going from 0.5 to 2.6 AU; hence these large bodies were formed from dust that, before its agglomeration, reached temperatures from 450 to 3000 K (Fig. 2). They were therefore still devoid of water and of any volatile fraction. The largest body of this zone, that is the protoearth, reached from 80 to 86% of its final mass at that time. This corresponds roughly to the size of its nucleus plus its deep mantle, defined by the well-known seismic discontinuity at a depth of 660–670 km (Jackson 1998).

The last 17% of the Earth's mass, which roughly correspond to its upper mantle, represent the results of the final stages of its accretion in which large objects were brought either from very hot places, closer to the Sun than 0.5 AU, where they had lost more of their volatile metals, or from colder places, beyond 2.6 AU, where the carbonaceous chondrites become more and more prevalent. Wetherill (1991) rightly argues that in the asteroid belt, very large chondritic objects can form and be later ejected by resonances with Jupiter's period; some might have hit the protoearth. The large size of these accreting bodies implies that it becomes a stochastic process involving a very small number of objects; hence, good predictions become impossible.

It remains, however, plausible that the total amount of water brought about by carbonaceous chondrites was not large. The composition of the upper mantle is known incompletely, mostly through rocks from volcanic eruptions. Wänke *et al.* (1983) conclude that, in the mantle, refractory elements are enriched by a factor of 1.3, moderately volatile elements are depleted by factors from 0.1 to 0.2, and very volatile elements are depleted by 2 to 4 orders of magnitude. No trace has been found yet in the upper mantle of any impact by a large chondritic asteroid. Mixing in the mantle is not well understood either.

In Delsemme (1991), I computed a model assuming that the asteroid belt originally contained 10 terrestrial masses, that ordinary chondrites contained no water, and that water in carbonaceous chondrites grew with their heliocentric distances in the belt (namely 1% in $C3$ chondrites, up to 3.2 AU; 3% in $C2$ chondrites, up to 3.8 AU; and 6% in $C1$ chondrites, up to 4.4 AU). This admittedly crude model suggests that we could not have accumulated much more than 200 m of a uniform layer of water on the primitive Earth. Claims that $C1$ chondrites may contain as much as 10% water have now been attributed to terrestrial water contamination (Chyba 1991). Even if I was mistaken by a factor of several, the water contribution from chondrites would remain very small in comparison to our oceans. At this stage of our enquiry, we could rightly wonder where all our water came from. We would not be alone to be puzzled. Clayton (1999) wrote: "some water remained in the inner regions of the solar nebula, where it was acquired by Earth and other rocky terrestrial planets, by processes that remain *largely unknown*" (my emphasis).

THE ROLE OF THE GIANT PLANETS

Let us remember first that two major scenarios had originally been proposed for the formation of the giant planets:

- either the immediate formation of giant gaseous protoplanets,
- or the accretion of their cores from solid planetesimals, followed by the gravitational capture of a large atmosphere from the gaseous nebula.

The first process assumes a gravitational instability in the nebula, whereas the second process implies that large solid cores were first collected by sweeping solid planetesimals. It was different from the agglomeration of the terrestrial planets only because the giant planets' solid cores were able to grow early to a mass large enough for their gravitation to capture giant gaseous atmospheres from the solar nebula (Pollack and Bodenheimer 1989).

The masses of the giant planets'solid cores have now been well determined (Hubbard 1984). They are all of about the same size, just beyond the minimum value required for the capture of a large atmosphere; this is a strong argument in favor of the second process. For this reason, the first process, which may still work for more massive objects (like double stars), is no more considered a serious possibility for the primitive solar nebula. In the second process, this is no more a coincidence that large solid embryos start outward from the distance of Jupiter, because water and volatiles condense onto solid grains and make much heavier planetesimals at that very distance (Fig. 2); these heavier planetesimals are of course comets because of their high content of water (40–50%) and of more volatile material (10–20%).

The growth process of these embryos was quantitatively described by Safronov (1969, 1972). Safronov uses his approach to explain the origin and compute the mass of the Oort cloud. He shows in particular that the mass of the comets available in the giant planets'zones is probably 6 or 7 times the mass of the solid embryos of the giant planets. During the agglomeration of these solid cores, as soon as one of them reaches a size of a few terrestrial masses, most of the embryo-grazing comets that miss collision are ejected at hyperbolic velocities to infinity. Jupiter has ejected to interstellar space more material than any other planet, whereas more than half of the Oort cloud mass was supplied by Neptune, but only 4% by Jupiter (Delsemme 1999).

Since the comets were ejected at random, a sizeable portion of them escaped by first crossing the inner Solar System, bombarding all objects, planets, and satellites that were in their path, and bringing water and volatile elements to the rocky terrestrial planets. How does this process compare to the late stages of accretion from rocky planetesimals onto terrestrial planets? It deals with a much larger initial mass and implies much larger (hyperbolic) velocities for the collisions with the terrestrial planets.

HYPERBOLIC VELOCITIES

Using recent data (Hubbard 1984), I found a total of 74 Earth masses for the solid cores of the giant planets, meaning that the total mass of the comets that had accreted in the zones of the future giant planets was between 400 and 500 Earth masses (Delsemme 1992d). This enormous amount must be compared with only a few (less than four or five). Earth masses in the region of the terrestrial planets. Using Safronov's model (Delsemme 1995b) I also found the root-mean-square (r.m.s.) relative velocities, at steady state, of those comets that were considerably deflected when they barely missed an impact with a growing embryo. These velocities grow in proportion to the growing size of each embryo. They reached up to 35 km/s with the embryo of Jupiter, 30 km/s with that of Saturn, 27 km/s with that of Uranus, and 28 km/s with that of Neptune. These relative velocities must of course be added vectorially to the orbital velocity of each giant planet.

The comets that were ejected in orbits going in the direction of the terrestrial planets had their velocity increased by their fall to the Sun, so that those that hit the Earth had an average r.m.s. velocity beyond 42 km/s. Most of the collisions with the Earth will produce ejecta velocities beyond the escape velocity from the Earth. Of course my model is simplistic (Safronov's θ is assumed to be 1 and the velocity distribution supposed to be normal) but it helped me to understand that the process was very inefficient; comets had to bring many times more water than the present amount of seawater.

I had not yet understood these features when I published (Delsemme 1991) a minimal assessment of the amount of water brought to Earth by Jupiter's and Saturn's zones. I assumed wrongly that, in a first approximation, I could neglect Uranus and Neptune. I could already explain *twice* the amount of water present in our oceans, and an efficiency of 50% did not look unlikely to explain the ejecta to space of each collision. Later (Delsemme 1992c), I completed my model with the comets coming from the zones of Uranus and Neptune and also enlarged the masses of the solid embryos used by Safronow, with better data coming from Hubbard (1984). My new result is six times the amount of our seawater. This is consistent with the large hyperbolic velocities of comets scattered by the growth of the giant planets' embryos. Later, I inadvertantly introduced a numerical mistake in the model and found 16 times the amount of seawater! The mistake is repeated again in Delsemme (1997). Table II gives the correct figures.

This is also consistent with a large atmospheric erosion, which implies giant vapor plumes after practically each cometary impact. Melosh and Vickery's (1989) model of the mass of a vapor plume is consistent with my results, with the understanding that their model as well as mine are rough approximations. Other evaluations confirm the order of magnitude of my results. Matsui and Abe (1986) find that comets brought down to Earth four times as much water as the present mass of our oceans. Fernandez and Ip (1983) have revised upward Safronov's evaluations; Ip and Fernandez (1988) find now ten times as much water as the mass of the oceans. Consistency is achieved since our results are all within a factor of 2 of the mean.

Table II also shows that more than 85% of the total amount of seawater comes from Jupiter's zone. More recently, I showed (Delsemme 1999) that the correct figure is 87%, by using Matsui and Abe's (1986) orbital data. This neglects the events

TABLE II
Thickness of Uniform Layer Brought to Earth by Late Impacts

Origin of layer	Chondritic silicates	Water	Carbon compounds	Atmosphere
From carbonaceous chondritic asteroids (2.6 to 4.4 AU):				
	2.0 km	0.20 km	0.10 km	—
From comets that accreted in the zones of:				
Jupiter	3.0 km	11.0 km	4.0 km	600 bars
Saturn	1.0 km	3.0 km	1.0 km	140 bars
Uranus	0.15 km	0.5 km	0.15 km	23 bars
Neptune	0.06 km	0.2 km	0.06 km	10 bars
Totals	6 km	15 km	5 km	770 bars

Note. Specific gravities assumed to be 2 for carbon compounds and 3 for silicates. The water layer is 5.8 times the amount of our oceans. These estimates do not take either impact erosion or the Moon formation into account (from Delsemme (1992c)).

that induced the formation of the Moon, which will be discussed later. At any rate, our discussion implies that the isotopic features found in seawater are mainly derived from comets that originated in Jupiter's zone.

THE LUNAR IMPACT RECORD

The Basaltic Volcanism Study Project (1981) confirmed the similarity of the cratering on the Moon, Mars, and Mercury. In particular, the density distribution versus size of the craters was similar on the three bodies. It confirmed that the cometary bombardment was massive and took place early and about at the same time for the three bodies. The lunar impactors' mass was much too large in the first 700 million years to be explained only by the mass of protoplanetary bodies (Wetherill 1980) formed in the inner Solar System.

The only accurate chronology was drawn from lunar data. The lunar rocks brought back by the Apollo and the Luna missions have been dated by their radioactive isotopes (a measure of their solidification ages). This provides the dates at which different regions of the Moon were still covered by liquid lava that had obliterated any trace of the previous craters; hence, it is the time from which the cumulative counting of impact craters can be done. These data were published by the Basaltic Volcanism Study Project (1981). I used them (Delsemme 1997) to compare the cratering rates on the Moon with a model of the orbital diffusion of comets coming from the different zones of the four giant planets. For this purpose, I needed first an approximate chronology of the Solar System. Table III shows the adopted chronology. This table also shows the half-life for the depletion of the comets' numbers in the different zones of the giant planets, coming from their orbital decay.

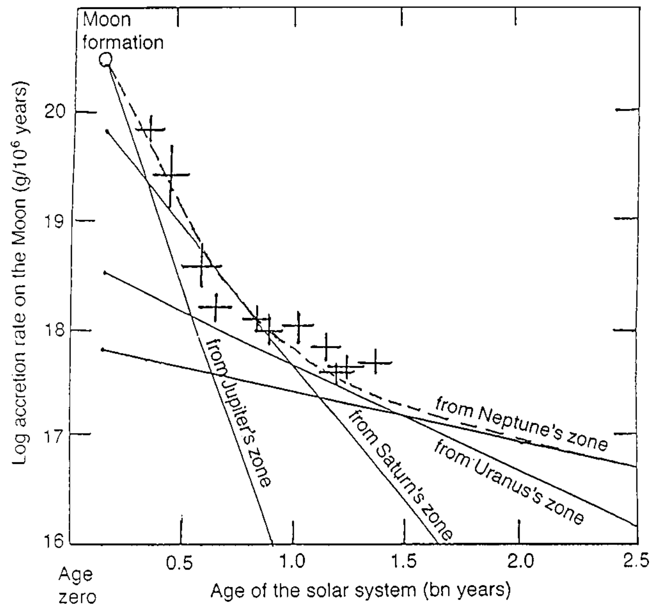

FIG. 3. The cumulative flux of the lunar impacts has been deduced for different regions of the Moon from the observed crater density. The radioactive age of lunar rocks brought back to Earth gives the epoch at which previous impacts were erased by molten lava. The four straight lines are the four exponential decays of the comet fluxes coming from the zones of the giant planets. After the first billion years, the total rate of lunar impacts is about a factor of two higher than the cometary contribution (dotted line), suggesting a cumulative asteroidal contribution of 2×10^{21} g.

TABLE III
Time Scales for the Early Solar System

Chronology for the beginning of the planetary system	
Dust sedimentation from gaseous disk (4.56 B years ago, deduced from chondrite ages)	Age zero
Largest planetesimals reach 10 km	10 000 years
Size distribution of planetesimals, 50 to 500 km	100 000 years
Runaway agglomeration for Jupiter's embryo	1 million years
Thirty-odd protoplanets (from Moon to Mars size) in the zone of the terrestrial planets	1 million years
Runaway agglomeration for Saturn's embryo	2 million years
Dissipation of nebular gas finished for 98%	5 million years
Runaway agglomeration for Uranus' embryo	7 million years
Runaway agglomeration for Neptune's embryo	14 million years
Earth's core formation (Earth's accumulation is finished for 85–90%)	42 million years
Formation of the Moon (grazing impact)	50 million years
Half-lives for orbital diffusion	
Comets from Jupiter's zone	50 million years
Comets from Saturn's zone	120 million years
Comets from Uranus' zone	300 million years
Comets from Neptune's zone	600 million years
Cometary bombardment of Earth, complete for 99%	1 billion years

Note. The dates for the Earth's core separation and the Moon's formation are in agreement with recent radioactive determinations (Lee *et al.* 1997).

Only the half-life in Jupiter's zone was computed; the other half-lives were assumed to be in proportion to the orbital periods of the giant planets. This model is shown in Fig. 3. The four straight lines on this logarithmic diagram show the exponential decay of the cometary impacts coming from the four different zones of the giant planets.

The sum of these four exponential decays is shown by the dotted line. The crosses are the cumulative rates of impact cratering published by the Basaltic Volcanism Study Project (1981). These crosses represent error bars: vertical for crater counting and horizontal for the date when previous craters were erased by lava. The good fit of the model for the first billion years is helped by the logarithmic scale, and an accuracy of a factor of 2 on the cometary masses may still be wishful thinking. However, the very large intensity of the lunar impacts seems to be correctly predicted at least for the first 700 million years; the contribution of stony (asteroidal) bodies to lunar impacts, even if it existed, is completely hidden by the huge intensity of the cometary contribution during most of the first billion years. After this epoch, crosses are consistently higher than the cometary model, suggesting a rather steady "asteroidal" contribution of about 5×10^{17} g per million years. It is obvious that the Earth and the Moon are sufficiently close to each other to have shared the same density of cometary and asteroidal impacts (with proper corrections for the different gravitations). Here on Earth, erosion and weathering have obliterated all telltales of this early bombardment. Lunar impact cratering is the best empirical evidence of what happened on the Earth during the first billion years of its existence.

Chyba (1987, 1991) has published extensive discussions on this very subject matter. His statement that the oceans would have been filled during the first 700 million years if only 10% of the impactors had been comets can be interpreted as meaning that if 60% of the impactors were comets, then six times the amount of seawater would have been brought down to Earth. This is consistent with my results. Chyba seems to be reluctant with this conclusion, because he demonstrated the difficulty of ejecting large masses of water from the Earth to space. This is true only if hyperbolic comets are ignored; Safronov's mechanism implies a very large fraction of hyperbolic comets that passed only once through the inner Solar System before being permanently lost to space. This being taken into account, there are now four independent models that concur with the fact that four to ten times the mass of seawater was brought down to Earth by comets ejected by the growth of the giant planets' embryos.

HEAVY NOBLE GASES

I have also discussed (Delsemme 1997) the empirical confirmations derived from geochemistry and geology. There are first the isotopic patterns shown in our atmosphere by the abundances of krypton and xenon. Their independent fractionations can be explained only by a low-temperature trapping in ices. An extreme form of gas trapping is the existence of gas clathrates. Their presence in comets has been proposed (Delsemme and Swings 1952) to explain why comets simultaneously release gases with very different vapor pressures at the same heliocentric distance, which otherwise is inexplicable. The general problem of gas adsorption by snows was studied in the lab by Delsemme and Wenger (1970) and in comets by Delsemme and Miller (1970). Bar-Nun *et al.* (1988) and Bar-Nun and Kleinfeld (1989) have confirmed our interpretation by studying in the laboratory the clathrate enrichment factors of the isotopes of krypton and xenon at the temperatures of 30 to 75 K expected in the outer ranges of the Solar System. Owen and Bar-Nun (1993) remark that our atmosphere cannot have been entirely formed by comets in that temperature range, because krypton and xenon are not abundant enough in our atmosphere.

Indeed, only 8% of the comets came from Uranus' and Neptune's zones; 12% came from Saturn's zone, where they accreted at a temperature of about 130 K (see Fig. 2) and 80% from Jupiter'zone (225 K). At such a temperature, the icy grains had ample time to vaporize their noble gases before accreting into comets. The important fact is the separate patterns of the isotopic distribution for krypton and for xenon, coupled with the xenon to krypton ratio that cannot be explained by anything but clathrates (or trapping in amorphous ice, which produces the same result); in particular, any sizeable contribution from carbonaceous chondrites is ruled out in our atmosphere by the present results (Swindle 1988).

SIDEROPHILE METALS

Comets brought to Earth not only water and gases, but also a thin veneer of siderophile metals in cosmic proportions. These metals were brought to Earth after the formation of its iron core (see Table III). This explains why these metals were not melted with iron to disappear into the Earth's core. If it had happened, siderophile metals would have been irregularly depleted in the crust where they would have lost their cosmic relative proportions. Chyba (1991) has carefully discussed the terrestrial mantle siderophiles; however, he points out that numerous uncertainties render exact (numerical) comparisons pointless. I agree: the only solid ground is the cosmic relative proportions, which establish that siderophile metals were brought to Earth by a cosmic process at a more recent time than the Earth's core formation.

THE PRIMEVAL BIOSPHERE

Comets brought an average of 45–50% water by mass (and possibly more for the comets brought from Jupiter's zone); 13–16% of volatile compounds containing carbon including CO, CO_2, and volatile organics (4–5% with N), plus 13–15% of refractory organics, and 22–26% of silicates. Table II (Delsemme 1997) shows that, after water condensed into the oceans, the atmospheric pressure would still have reached an extremely high value if the formation of solid carbonates had not already begun. Under high pressure, CO_2 is increasingly soluble in rainwater, becoming carbonic acid H_2CO_3. During the slow cooling of a very hot early atmosphere, long-lasting torrential rains transformed silicates extant in rocks into solid carbonates, mostly limestone (carbonate of calcium) and dolomite (carbonate of calcium and magnesium).

Major ancient sediments of limestone and dolomite exist that are 3.8 billion years old, for instance in the southwest of Greenland; they are among the most ancient sediments known. If all the ancient sediments were heated enough, they would form an atmosphere of CO_2 comparable to that of Venus (Delsemme 1992b, 1998b). The higher temperature still extant on Venus explains why the total amount of CO_2 brought by comets is still in its atmosphere and not in carbonate rocks.

The most characteristic feature of an early atmosphere derived from comets is its intermediate state of oxidation and reduction (its redox ratio, as chemists say), which is maintained by the steady arrival of more comets during the first billion years. When the cometary bombardment subsides, photodissociation of many molecules by the solar ultraviolet in the upper atmosphere releases hydrogen that steadily escapes from the exosphere, changing very slowly the redox ratio to more and more oxidations and less and less reductions. The early conditions were particularly favorable for the emergence of life, as soon as the environment was no more hostile to its survival.

After a while, the two prevalent molecules extant in the atmosphere were more and more CO_2 and less and less CO. The solid carbonate formation made the atmospheric pressure drop drastically, which considerably increased the relative proportions of nitrogen.

THE DEUTERIUM EVIDENCE

Deuterium is an unstable isotope at thermonuclear temperatures, in the sense that it burns easily to form helium. Its mere presence in the Universe is an anomaly that has only been explained by the hot Big Bang theory. In the Big Bang, around one billion degrees, hydrogen first formed a very large amount of deuterium, which combined immediately with itself to form helium. However, the quenching of the Big Bang was too rapid to reach a thermonuclear steady state. This left traces of uncombined deuterium, probably more than 20 but less than 30 ppm (parts of deuterium per million hydrogen). This is the origin of all the deuterium still in existence.

Since deuterium cannot be created any more, but can burn easily inside stars, its abundance has diminished irregularly. There is still a variable abundance of 5 to 15 ppm of deuterium in nearby interstellar clouds. However, the atmospheres of Jupiter and Saturn bear witness that its abundance, when these atmospheres were captured some 4.5 billion years ago, was still close to 20 ppm. Our seawater contains about 160 ppm of deuterium, that is, an enrichment of about eight times, in respect to the hydrogen of the solar nebula. This enrichment probably remains the best clue that the total amount of seawater was brought to the early Earth by comets.

For water, two types of enrichment processes must be distinguished. The first one exchanges neutral atoms or molecules, whereas the second one uses ions to exchange electric charges. All neutral exchange reactions are very sluggish at cold temperatures, because they all have potential energy barriers that can be overcome only by heat. In ion–molecular reactions, the high ionization energies easily cross these barriers; hence the reactions remain fast down to the vicinity of the absolute zero. For this reason, they are effective in interstellar space. However, neutral reactions may accelerate millions of times if they are helped by an ionizing radiation.

The only known source for the deuterium enrichment in seawater is the same as in comets and meteorites, namely, the enrichment of water frost covering the interstellar grains. This enrichment process is understood for water. However, in interstellar space, many ion–molecular reactions compete and some of their rate constants remain uncertain. Finally, the kinetics of many reactions have such large time constants that the chemical steady-state may never be reached. At the present time, all that can be said is that the enrichment in deuterium of the frost covering interstellar grains is high; it is certainly more than tenfold but could easily reach 20-fold.

From this discussion, it makes sense to accept that the deuterium enrichment observed in the water of recent comets (Halley, Hyakutake, and Hale–Bopp) is that of the frost of interstellar grains that have been kept cold enough, before being agglomerated into chunks large enough not to exchange deuterium with the outside gas. This would be the case for comets that accreted in the zones of the outer giant planets or beyond in the Kuiper Belt. It so happens that 96% of the comets arriving from the Oort cloud originated in the zones of the outer giant planets (Delsemme 1999).

Since the deuterium enrichment in the water of three recent comets is the same, within the error bars, we accept the value found for Comet Halley, which has been particularly well measured *in situ*. This enrichment is close to 320 ppm, that is 16 times that of hydrogen in the protosolar nebula (using the atmospheres of Jupiter and Saturn as a reference). This is twice as much as seawater, which is close to 160 ppm, or 8 times the primitive nebular hydrogen. A few years ago, astronomers who found this discrepancy were reluctant to accept that comets were the only source of seawater, and several popular reviews propagated that doubt.

The second source of seawater still was comets, but of a different kind (Delsemme 1998d, 1999), since they agglomerated in Jupiter's zone; not only were they formed in a warmer zone than the other comets, but they created a *cold wall* that condensed all steam vaporized in the hotter zones of the inner Solar System (Stevenson and Lunine 1988, Cyr *et al.* 1998). There, the deuterium enrichment was six (Fig. 4, from Geiss and Reeves 1981).

At the temperature of Jupiter's zone (about 225 K, from Fig. 2) neutral-exchange reactions are rather sluggish. However, the steam coming from the hotter zones of the inner Solar System (where neutral-exhange reactions were much faster) had already been depleted in deuterium down to an enrichment between 2 and 3 (from Figs. 2 and 4). Standing in contrast, because of the sluggishness of the neutral-exchange reactions, the icy mantles of the interstellar grains still present in Jupiter's comets had their deuterium enrichment depleted only to an intermediate value between 16 and 6. As indicated by the two opposite arrows on Fig. 4, the steady-state value of 6 acted as a common attractor on the two fractions. Even if none of the two fractions reached their steady state, it is likely that the mixture was very close to 6.

Another scenario is to reach rapidly the chemical steady state by the use of far-ultraviolet or X rays from the early Sun. If any ionizing radiations hit the relevant snows at any time, their charge-exchange reactions act as a catalyst and the kinetics is accelerated by a huge factor (typically, millions of times). In this case, the kinetic constants measured in the laboratory for neutral-exchange reactions by Lécluse and Roberts (1994) cannot be used any more and the steady-state value of a sixfold deuterium enrichment is immediately reached in Jupiter's zone on snows of any origin.

Hence, whatever the scenario, there is not much doubt on the fact that comets from Jupiter's zone had a deuterium enrichment of sixfold. We have not yet observed any; most were ejected on

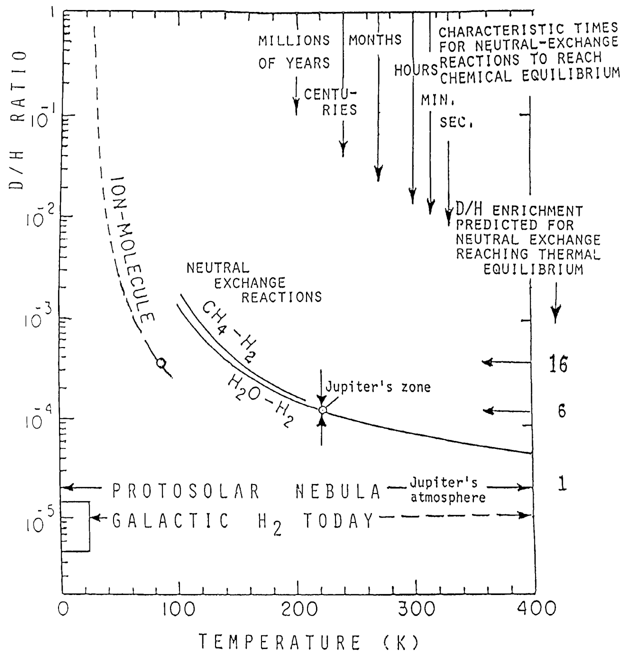

FIG. 4. Deuterium enrichment in water (and in methane) in respect to protosolar hydrogen (represented by its 20 ppm ratio measured in Jupiter's atmosphere). Its temperature dependence from neutral-exchange and ion–molecular reactions comes from Geiss and Reeves (1981). The curves are the chemical equilibrium values. The D/H enrichment of 16 is the mean in recent comets. An enrichment of six is predicted for the chemical steady state of Jupiter's zone comets, whatever the origin of their water–snow mixture or the kinetics of the deuteriun-exchange reactions; 80% of Jupiter's comets and 20% of other comets (predicted by geometry) produce seawater.

hyperbolic orbits to interstellar space, and comets coming back from the Oort cloud include only 4% of them (Delsemme 1999). Eventually, we will observe one of them, if we are patient.

FORMATION AGE OF THE MOON

The deuterium enrichment of seawater has been influenced by the formation of the Moon because Jupiter's comets that first made the bulk of the early Earth's bombardment subsided much faster than the comets from the outer planets (their half-life for orbital diffusion was 50 million years only, see Table III). For this reason I computed (see Table IV) the mixture of the seawater coming from Jupiter and from the outer planets as a function of the epoch of the Moon's formation. This assumes that the catastrophic impact that formed the Moon also ejected all the water preexisting on the Earth before that date. The last column of Table IV also gives the residual deuterium enrichment of our seawater.

TABLE IV
The Eightfold Deuterium Enrichment of Seawater Puts Limits on the Formation Age of the Moon

Epoch of moon formation	Share of seawater's origin: From Jupiter's	Share of seawater's origin: From outer planets	Final D/H enrichment
0	87%	13%	7.3
50 M yr	80%	20%	8.0
100 M yr	73%	27%	8.7
150 M yr	65%	35%	9.5
200 M yr	55%	45%	10.5
250 M yr	45%	55%	11.5

Note. This result is in agreement with a recent determination of the Moon's formation age from radioactive data: (50 ± 10) M yrs obtained from lunar rocks by Lee *et al.* (1997). Age zero is defined in Table III.

The observed eightfold enrichment of seawater constrains the time when the Moon's formation vaporized all the oceans. It is 50 million years after dust sedimentation. This result is in good agreement with a recent determination of the Moon's formation age from radioactive data, namely (50 ± 10) million years, obtained from lunar rocks by Lee *et al.* (1997). Using the uncertainty of this determination to compute the error bar, I find a predicted deuterium enrichment for seawater of (8.00 ± 0.14), which coincides well with that measured for standard mean ocean water $(7.8 \pm 0.2$, Delsemme 1999).

SUMMARY OF THE EVIDENCE

- First, the evidence is based on the existence of massive solid cores of high Z material in the giant planets, all of about the same size. These cores can be best explained by the accretion of solid grains that sedimented to the mid-plane of the nebular disk, exactly as for the terrestrial planets. The four solid cores were massive enough to attract a large gaseous atmosphere; it did not occur completely for Uranus and Neptune only because of the early dissipation of the nebular gas (see Table III).
- The building of these massive solid cores from comets that accreted in the giant planets'zones provides a mechanism to bring water and other volatiles onto the terrestrial planets. Comets were deflected on hyperbolic orbits by the growing cores, and they mostly escaped to outer space. A fraction of them escaped through the inner Solar System, but some hit the inner planets. In spite of the inefficiency of the collisions, their mass was large enough to bring all the water and volatiles on the terrestrial planets.
- The cratering record on the Moon, Mars, and Mercury confirms this early massive bombardment, which must have reached the Earth as well.
- The lunar cratering shows exponential decay rates consistent with the decay of the comet numbers coming from the giant planets' zones.
- The large mass of the early lunar bombardment is consistent with the comets' mass coming from Jupiter's zone.
- The nature and the amounts of the volatiles brought about by comets are consistent with the atmospheres of the Earth, Venus, and Mars (taking into account their different evolutionary histories) as well as with the traces of frozen water found near the poles of the Moon and Mercury.

- The comet bombardment also explains the origin of all carbon extant on Earth in solid carbonate sediments as well as in organic compounds.
- It also explains the late origin of the siderophile metals in the Earth's crust and upper mantle. These metals are in cosmic proportions; this implies that they arrived late enough not to have been depleted by the formation of the Earth's core, in spite of their affinity for iron. Their total amount on Earth or on the Moon is not known with accuracy and hence cannot be compared with the cometary bombardment.
- The anomalous and decoupled fractionations of the six isotopes of krypton and of the seven isotopes of xenon in our atmosphere cannot be explained by any evolutionary history on the Earth, but only by their trapping in snows at the low temperatures of cometary formation (30–75 K), in the zones of Uranus and Neptune. Moreover, the large amount of comets that accreted at 225 K in Jupiter's zone and the smaller fraction near 130 K in Saturn's zone may explain the low abundance of krypton and xenon in our atmosphere. Since observational data on krypton and xenon in comets are missing, their accurate abundances in the atmosphere cannot be predicted; however, the evidence based on their anomalous ratio is compelling.
- Finally, the deuterium enrichment of seawater remains one of the best signatures of the cometary origin of our biosphere. Its interstellar enrichment was modified in the comets of Jupiter's zone, possibly by the condensation of steam vaporized in the hotter zones of the inner Solar System or, alternately, by using the catalytic effect of far ultraviolet or X rays of the early Sun. The deduced formation age of the Moon agrees with recent radioactive data.

DISCUSSION

The large mass of the solid cores of the giant planets is a sure warrant that a bulk of solid icy planetesimals (that is, comets) accreted from interstellar grains in the outer zones of the Solar System. The orbital scattering and ejection of comets during the agglomeration of the solid cores is a direct consequence of it, but neither the total mass of ejected comets nor their relative velocity distribution (Safronov parameter θ, close to 1) is known with accuracy. Mass estimates from impact sites on the terrestrial planets and the Moon cannot be assessed with much accuracy either, although they are consistent with a major cometary bombardment, within the first billion years. This is also consistent with our atmosphere, our seawater, our organic compounds, and the cosmic proportions of our siderophile metals.

Consistency is not proof. At least a fraction of the impactors can be asteroids or even planetary embryos (Wetherill 1991) detached from the asteroid belt by resonances with Jupiter's period of revolution. What is the importance of this fraction? As far as its mass is concerned, it could easily explain a rather large amount of our outer mantle, but the real question is rather to know the fraction of our waters, carbon, nitrogen, and atmosphere that did not come from comets, but from carbonaceous chondritic asteroids. My model shown in Table II finds that only 1% of water came from such a source. Of course, we must remain wary of such models; what is the observational evidence?

We mentioned earlier in the section on Radial Mixing that in the mantle the refractory elements are enriched and the volatile elements are depleted with respect to chondritic ratios. No trace has been found in the upper mantle of any impact from a large chondritic asteroid.

There are, however, two quantitative proofs that a very large fraction of our biosphere has been brought to Earth by comets only:

(1) our correct prediction of the deuterium enrichment in seawater,

(2) the explanation of the atmospheric ratios of krypton and xenon.

The first proof is rather decisive. The 16-fold enrichment of deuterium has been accurately measured in the water of Comet Halley, and the sixfold enrichment at 225 K has been established from the accurately known thermodynamic equilibrium in the exchange reaction:

$$H_2O + HD = HDO + H_2.$$

The temperature of 225 K is based on empirical data (Fig. 2). It is not critically sensitive (Fig. 4). The initial ratio of 87/13 is based on the orbital geometry of the giant planets. A few hundred million years later, the random walk of comets among the outer giant planets (Weissman 1999) may blur their origin and change their rate of capture in the Oort cloud, but this is not relevant to the initial geometry that produced the early terrestrial impacts.

The smaller ratio of 80/20 comes from the age of the Moon, independently established from radioactive data (Table IV). Hence the (8.00 ± 0.14)-fold enrichment predicted for seawater is reasonably accurate; its agreement with observations would disappear if another significant source of seawater had a different deuterium enrichment. Of course, some $C1$ chondrites, coming from the outer fringe of the asteroid belt, might also contain water with a similar deuterium enrichment. This may become a matter of semantics, because these chondrites might be chemically indistinguishable from the comets originating in Jupiter's zone (typically from 4.4 to 6.0 AU).

Incidentally, the lower deuterium enrichment of seawater, with respect to that of recent comets, indicates that interstellar grains exchanged their deuterium freely with the nebular hydrogen, without being impeded by their enclosure inside larger bodies. This is the first observational proof that these grains reached the nebular disk before accreting into larger chunks (the comets).

The second proof that our biosphere came mainly from comets is the oddity of the krypton/xenon ratio that has not been explained by any other process, but an adsorption in very cold cometary ices that must come from Uranus and Neptune's zones.

The dilution of these noble gases in our atmosphere is in agreement with the scenario that, when the frosty interstellar grains reached the zones of Jupiter and Saturn, they had already become too warm and had released their noble gases before their accretion into larger chunks.

The possibility of a radial migration of the outer giant planets soon after their formation has been reconsidered by Thommes *et al.* (quoted by Owen via oral communication at the Hawaii Meeting on Bioastronomy, IAU Commission 51 in August 1999). Its consequences for our scenario seem to be negligible; Jupiter is too massive to have migrated significantly; the other embryos must have accreted between 10 and 15 AU, implying that the 87/13 ratio should start at 85/15 (Table IV). But this effect diminishes during the radial migration of the outer planets and must have become negligible after 50 million years (formation of the Moon).

The oddity of the Kr/Xe ratio comes from interstellar space; it can be preserved at 15 AU by a slow desorption kinetics during cometary accretion, but partial desorption may also explain its dilution in the Earth's atmosphere.

Finally, theoretical difficulties in accreting large cores for the giant planets, as well as new doubts about their core masses, have led Alan Boss and others to reexplore the alternative of gravitational instabilities to trigger the formation of the giant planets. Even if this new paradigm is true, comets are needed to explain the excess of heavier elements in giant planets' cores, as well as the existence of the Oort Cloud; hence the source of the biosphere is likely to remain unchanged.

However, I think there is an easy solution to the theoretical difficulties. Models do not take into account that the accreting objects are comets that contain at least 60% water and volatiles. In each zone, there will be first several growing embryos; before any of their masses reach that of the Earth, the heat previously dissipated by early impacts will have vaporized a massive and extended atmosphere around each of them, which will dampen the velocities of grazing objects.

Hence the growing gravitation of the embryos will not scatter their relative velocities *enough* to make them fling apart; they will finally merge to form a single large core. I hope a theorist will use my suggestion to check that the large cores of the giant planets may indeed form.

CONCLUSION

The past 25 years have brought more and more evidence that an intense bombardment of comets has brought to the Earth most of our seawater, most of the volatile gases present in our atmosphere, and most of the carbon extant in the carbonate sediments as well as in the organic molecules used by life. In short, our biosphere has been brought by comets, allowing life to emerge as soon as the conditions were no more hostile to its survival. This explains why life emerged so soon.

The process could have occurred many times on rocky planets elsewhere in space. The existence of cold giant planets, accreting at those distances where comets may agglomerate, might be a necessary condition for the emergence of life elsewhere in the Universe, because they might be needed to scatter comets able to make biospheres (Delsemme 1995a).

In these highly personal reminiscences, I could not mention the large number of scientists whose work has influenced my thinking and shaped my ideas. The slow progress in science is like the assemblage of a gigantic jigsaw puzzle involving too large an amount of players, in particular when we deal with an interdisciplinary approach like this one. The cometary origin of the biosphere is an idea that has come of age in the second half of the 20th century and which seems now rather well established. Of course, nothing is ever certain in science, since its progress is steadily reached by trial and error. Last year's doubts about the origin of the deuterium enrichment in seawater are a good example of the process. I am glad to have clarified the situation.

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