COMETARY ORIGIN OF CARBON, NITROGEN AND WATER ON THE EARTH

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Abstract. Two independent assumptions are substantiated; firstly, that the Earth accreted from dust particles that were hot enough not to contain any volatiles; secondly, that after the accretion was finished, all the volatiles of the biosphere, including the atmosphere and the oceans, were brought by a cometary bombardment.

The first assumption is based on the empirical evidence that the planets originated from minor bodies. These minor bodies were generated by accumulation of fine dust particles, which sedimented from the gas of the solar nebula. We will demonstrate that, when the particles from the Earth's zone were separated from the nebular gas, they were close to 1000 K and at a thermochemical equilibrium with this gas. This implies that almost all carbon, nitrogen and water remained in the gas phase, respectively as CO, N_2 and steam. Since there was no volatile left in the minor bodies, they could produce neither atmosphere nor oceans.

The second assumption is based on the existence of the giant planets in the outer reaches of the solar system. Over there the solar nebula was very cold; the minor bodies were generated by accumulation of frosty particles and became cometary nuclei containing a large amount of ice and volatile stuff. When the giant planets' embryos reached a mass of 10 to 20 terrestrial masses, the orbits of billions of minor icy bodies were perturbed enough to send some of them to the inner solar system. A model shows that the icy bodies which hit the Earth are more than enough to explain the whole biosphere, including the atmosphere and the oceans.

Introduction

A significant amount of organic matter may have been brought onto the Earth by comets. This organic matter might have played a role in the emergence of life on the Earth. These two separate statements have both become less contentious than they were when I reviewed them ten years ago (Delsemme, 1981). It is my pleasure to recognize again John Oro's prescience in this respect.

However, I want to discuss here a much more drastic idea, brought by new developments in our understanding of the formation of the terrestrial planets in the protosolar accretion disk. This idea is that the *total* amount of carbon in our carbonates and the *total* amount of water in our oceans were brought about by a late bombardment of comets on an Earth almost devoid of carbon, of water and of all volatile and labile elements. We will see that the thickness of the cometary veneer probably implies ten or twenty kilometres of solid rocks which means that the crust and a small fraction of the upper mantle may also be of cometary origin. Convection in the upper mantle would have mixed all volatile and labile elements even much more deeply.

This may specifically describe the physical mechanism of the 'heterogeneous' process that has been invoked by some geophysicists to explain the formation of

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the Earth. We must be aware that neither the 'excess volatiles' nor the 'excess siderophiles' present on the Earth are easy to explain in geophysics. A recent paper by V. Rama Murthy (1991) suggests a possible explanation, based on a purely geophysical model, for the excess siderophiles. In this explanation, the excess volatiles remain unexplained. The traditional explanation that the Earth degassed massively in its early history has no empirical support because the oldest known evidence is more than one billion years younger than the age of the Earth. "During that 'lost interval' all the volatiles of the Earth could have been derived and recycled many times, while the evidence for the exact mechanism of supply was obliterated completely" (Turekian, 1972).

If the gas of the accretion disk had survived when the Earth's gravitation became strong enough, its capture by the gravitational field of the Earth could have produced what has become to be known as the 'primary' atmosphere, but the abundances of the noble-gas isotopes demonstrate that no trace of this primary atmosphere does exist today (Brown, 1952; Ozima and Igarashi, 1989). Either it was lost early, or it has never been captured to begin with (for instance, the solar gale of the T Tauri phase of the Sun may have blown away the solar nebula gas at an early stage). See a recent discussion in Sasaki and Nakazawa (1990).

Let's now summarize the history of ideas and models on the origin of the Solar System.

The Protosolar Accretion Disk

Laplace (1796) is the first who tried to solve the problem of the origin of the Solar System by using observational facts. In the last pages of his 'Exposition du Système du Monde' he writes that all the quasi-regularities of the Solar System suggest that a 'fluid of immense extent' enveloped the Sun 'as an atmosphere', whose original rotation enforced all those quasi-regularities. For a long time however, 19th century astronomers believed that Laplace was wrong, because the Sun turned too slowly to result from the central agglomeration of this 'solar nebula' (dubbed this way by a false analogy with what we call now spiral galaxies).

The problem of the slow angular momentum of the present Sun disappeared when the solar wind was discovered. Its spiral motion away from the Sun produces a magnetic brake that slows the solar rotation continuously. This phenomenon has removed the apparent contradiction with a very fast initial rotation.

Laplace's hypothesis came back in favor some fifty years ago, but it still was a speculative scenario difficult to analyze numerically. For instance, von Weizsäcker (1944) proposed to arrange the gas eddies in epicycles in order to explain the distances of the planets (Bode's law). His analysis was shown to be in quantitative disagreement with fluid mechanics, but it attracted the attention on a possible mechanism that had been neglected so far: *viscous* turbulence can dissipate energy and redistribute momentum in the primitive nebula. To make a long story short, the basic theory of the *viscous* accretion disk has been given by Lynden-Bell and Pringle (1974).

Numerical models have been developed, in particularly by Cameron (1985), Lin and Papaloisou (1985), Wood and Morfill (1988), Morfill (1988), Morfill and Wood (1989).

There are still difficulties. For instance, the origin of the rather high viscosity needed to dissipate the angular momentum has not been completely clarified. Its most likely source is a strong convection driven by gas turbulence. Gas turbulence in the disk is itself maintained by the gravitational collapse of the interstellar cloud that feeds the disk. However, there are other possible mechanisms. A gravitational torque (Larson 1984) could also dissipate angular momentum. Such a gravitational torque can be introduced by a spiral structure in the disk, or in general by mass distributions that are not axisymmetrical. If the gas is ionized enough, magnetic forces could also play an important role.

Without elucidating the cause of the viscosity, observations have given a sudden respectability to the theory that describes Laplace's 'Solar Nebula' by a *viscous* accretion disk. The ubiquity of accretion disks around *very young* stars is now supported by strong observational evidence. The Infrared Astronomical Satellite IRAS has found an excess of infrared radiation around many stars (Rowan-Robinson, 1985). This infrared excess is interpreted as coming from the thermal emission of a surrounding disk of cool dust. Many of these stars are very young T Tauri stars (Hartigan *et al.*, 1990). Some, like FU Orionis, are still probably accreting mass (Hartmann and Kenyon, 1990). Bipolar outflows are often present simultaneously. Finally, optical pictures in the visual have resolved dusty disks of size 500 to 1000 astronomical units (AU) like in Beta Pictoris (Smith and Terrile, 1984).

Numerical Models

Because of the supporting observational evidence, it has become reasonable to develop numerical models describing the origin of the Solar System as an accretion disk. There are two unknown parameters that can fortunately be combined into one. The first is the collapse time of an interstellar cloud nodule, to form the Sun through an accretion disk. Its order of magnitude only is known. Larson (1969) has established that, although the center of the nodule collapses fast, in order to accrete *one* solar mass, the outskirts of the nodule will reach the collapse center (that is, the accretion disk) 10^5 years later. Of course the actual rate of the collapse may vary somewhat because of density variations in the nodule, but it is useful to know that its average rate is of the order of 10^{-5} solar masses per year. In his evolutionary models, Cameron (1985) proposes accretion rates a few times larger in order to explain the high luminosities observed in very young T Tauri stars. This matter is of importance because the accretion disk has to radiate away the heat produced by the gravitational energy of the infall; hence, the larger the infall rate, the higher the temperature of the disk.

The disk viscosity is the other unknown parameter. It sets the dissipation rate of the inner angular momentum, hence the disk lifetime. By combining the uncertain

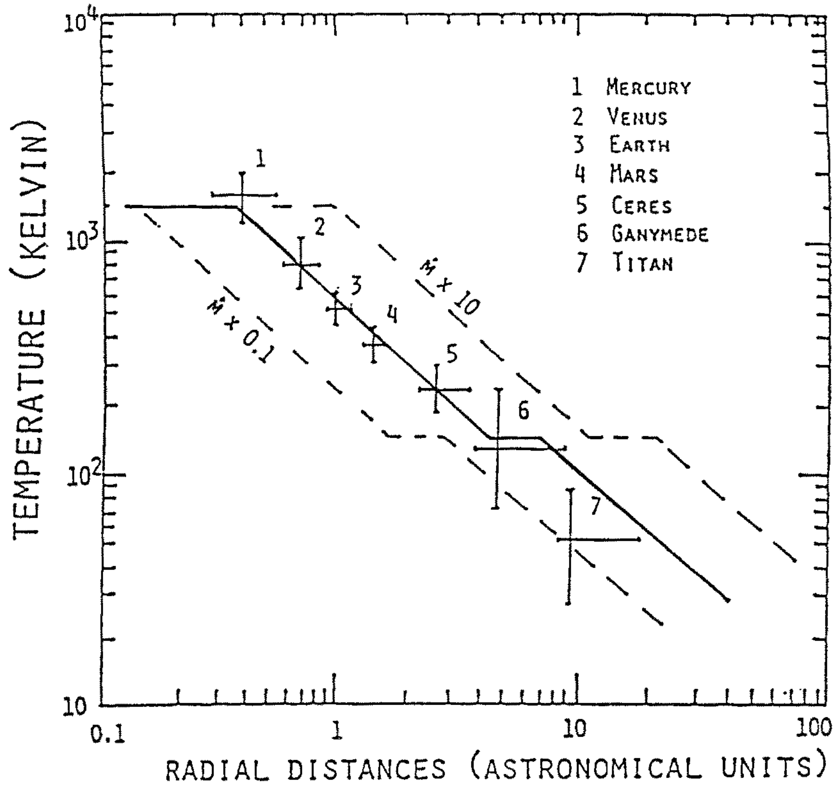

Fig. 1. Mid-plan temperature of the accretion disk as a function of radius. The solid line is the adjustment of the disk model (Morfill, 1988). The two dotted lines correspond to accretion rates 10 times smaller or larger. The crosses are Lewis 1974 aggregation temperatures of planets and satellites. These crosses do not represent error bars; they show the width of the zone from which planetesimals are collected, and their corresponding temperature range.

rate of collapse and the uncertain coefficient of viscous friction in one single variable, this variable can be adjusted to empirical data. It is important to realize that most models predict a temperature gradient in the disk which is not far from r^{-1} (r heliocentric distance). The adjustment of the parameter changes the temperature everywhere, but not its gradient. This gradient reflects the shape of the gravitational potential well, and comes as a consequence of the viral theorem.

Morfill's (1988) can be used as an example of a rather evolved model, where the mid-plane temperature in the disk varies with $r^{-0.9}$, except at temperature plateaus due to the condensation of two major constituents: silicates (within (0.4 AU) and water (from 4 to 8 AU).

The first empirical data we can use are the condensation temperatures of the planets established by Lewis (1974) from their mean densities. We'll come back to Lewis's model later, but we want to emphasize that the success of the disk adjustment to Lewis's temperatures comes from the smooth radial temperature gradient in r^{-1} used by Lewis for the condensation temperatures of the planets; see Figure 1.

The Chondrites as Clues to Planetary Formation

Empirical evidence on the way planetary bodies were formed is found in those primitive meteorites called chondrites. The chondrites are primitive because, at the exception of a few very volatile elements, most of their elements have remained accurately in the same abundance ratios as in the Sun. This establishes not only that they derived from the same primeval reservoir as the Sun's, but also that they have never been through processes of differentiation, such as those that have separated the cores from the mantles of most of the planets.

The chondritic meteorites come from the Asteroid belt, that is, roughly from 2 to 4 AU. This was established from accurate triangulation of three orbits of chondrite meteorites observed as meteors during their entry into the atmosphere and recovered on the ground later, supported by the orbits of about 30 bright meteors identified as chondritic but unrecovered later (Wetherill and Chapman, 1988). Chondrites are assumed to be fragments of asteroidal collisions. Their parent bodies were of the order of 100 km radius (this size is implied by their concordant radiogenic ages of 4 billion years or more, implying a fast cooling). This small size explains why they had no gravitational differentiation.

Chondrites are stony meteorites (made mostly of silicates) classified as carbonaceous, ordinary and enstatite chondrites according to their diminishing degree of oxidation. The enstatite chondrites are completely reduced and the carbonaceous chondrites are completely (CI, CM) or almost completely (CO, CV) oxidized. The most oxidized carbonaceous chondrites are those that contain the most volatile elements and in particular *very* large amounts of organic compounds (typically 6% carbon in CI). The chondrite classes seem to sample different regions of the accretion disk across the asteroid belt. Although the evidence is indirect, the infrared spectra of asteroids seem to imply that the dark C asteroids have carbonaceous chondritic surfaces, whereas the light S asteroids look more like ordinary chondrites see however the controversy about the identification of the S asteroids in Wetherill; and Chapman (1988). Another important clue comes from the fact that the C asteroids begin to outnumber the S asteroids at distances beyond 2.6 AU (Morrison, 1977).

The silicate matrix of chondrites shows that it was made by a moderate compression of dust grains of variable origins. In spite of their close contact, these often submicrometer-sized grains are chemically unequilibrated. For instance, oxidized grains touch reduced grains, some grains have been altered by liquid water and some have not, some refractory grains are in close contact with volatile grains. The matrix also imprisons larger objects, such as millimeter-sized chondrules or CAI (calcium-aluminum inclusions). The chondrules show signs of transient (and often partial) melting. The CAI are refractory grains probably made at temperatures higher than 1600 K.

This heterogeneous composition seems to imply a process entirely comparable to a sedimentation. In our rivers, when water turbulence subsides, sand sediments to the bottom, bringing together grains of quartz, feldspar, mica, calcite or silicates of widely different origins. Since chondrites have never felt the gravity of a large planet, this sedimentation must have taken place in the solar accretion disk.

This is exactly what our models predict. During the gravitational collapse of the interstellar nodule into the disk, the gravitational energy of the infall kept a high rate of turbulence in the gas. This turbulence kept the dust in suspension for some 10^5 years. But when the collapse rate subsided before completely stopping, there was a time when the dust was not supported any more by turbulent eddies and fell down to the mid-plane of the now quiescent disk: this is a *sedimentation* that is going to make thin equatorial dust rings around the Sun.

From Dust to Planetesimals

After sedimentation in the quiescent disk, the dust grains move on practically circular and coplanar orbits (their different thermal histories come from the previous turbulence in the gas). A few years ago, we thought with Goldreich and Ward (1973) that gravitational instabilities in the dust rings would suffice to make numberless planetesimals in a few years only. Now, Weidenschilling (1988) has

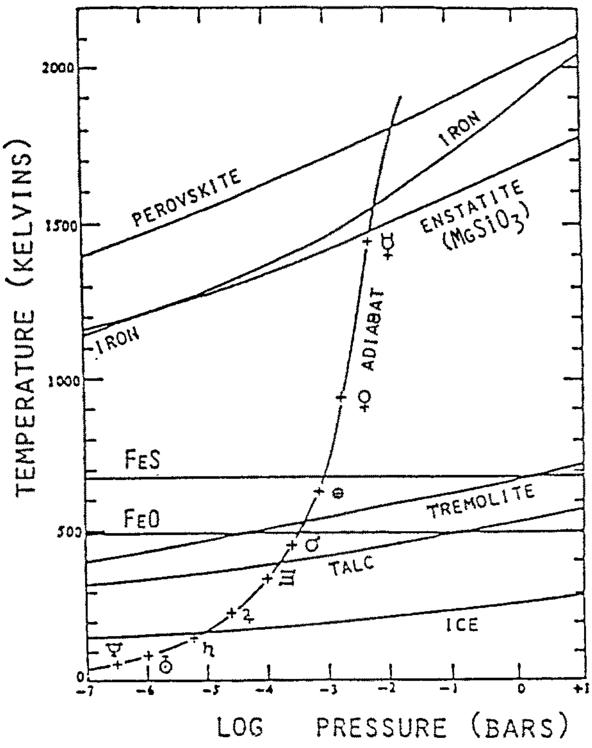

Fig. 2. Chemical condensation of minerals at thermochemical equilibrium in a gas of solar composition. The future positions of the planets are located along the adiabat representing the conditions in the accretion disk. The density of each individual planet is explained by the minerals that have already condensed at the temperature and pressure indicated by the planet symbol (from Lewis, 1972).

given solid arguments, showing that some turbulence is fostered in the dust ring by the small differential velocity existing between gas and dust; this low degree of turbulence is sufficient to prevent Goldreich and Ward's process. Weidenschilling concludes that planetesimals probably grew more slowly, by coagulation of grain aggregates that had endless soft collisions, due to different rates of settling and to drag-induced orbital decay. His mechanism can form meter-sized bodies in a few thousand years. Further growth from meter-to-km-sized bodies take again a few thousand years.

Thermochemistry in the Accretion Disk

It is time to come back to Lewis' (1974) approach which seems rather successful in predicting the different temperatures of formation of the Planets. Lewis starts from a mixture of elements in solar abundances at thermochemical equilibrium and at high temperature. Its cooling history shows the sequence of solid condensates that separate from the gas as it cools down. The thermochemical equilibrium is expressed in the pressure-versus-temperature plane (see Figure 2). It can be crossed by an adiabat describing a model of the accretion disk. The density of the different planets is then moderately well explained by the assemblage of the minerals that have already condensed at the position of each individual planet on the adiabat.

It is clear that a thermochemical equilibrium in a cooling gas does not accurately describe the scenario discussed previously. The success of the model comes from

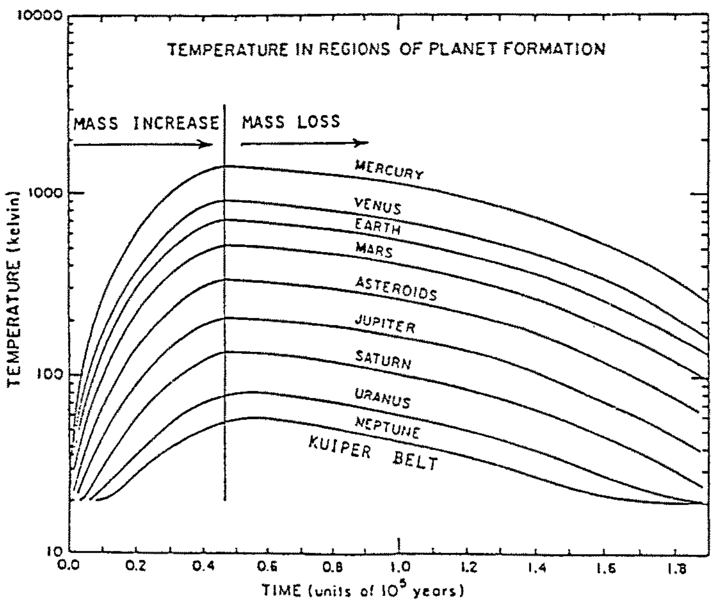

Fig. 3. Evolution of the temperature of the gas in the accretion disk, as it varies with time in the different zones of planet formation. In this model, the collapse of the interstellar cloud stops at the vertical line and the disk starts loosing mass as it still feeds the protosun (from Cameron, 1978).

the fact that a thermochemical equilibrium remains the same in a cooling sequence or in a heating sequence, and the evolution of the temperature in the accretion disk probably looked more or less like in Figure 3 (borrowed from Cameron's (1985) work for illustrative purpose only). The actual behavior of the disk was possibly more complicated than this; for instance there might have been irregular temperature peaks corresponding to a variable collapse rate at different times; dust sedimentation occurred either at the position of the vertical line (where the collapse was turned off in Cameron's model) or later (if the collapse rate diminished steadily) when a threshold was reached, below which turbulence had subsided enough not to be able to support the dust any more.

The success of Lewis' model also came in part from the fact that on Figure 2, most of the solid/vapor transition temperatures show a rather insensitive pressure dependence. For this reason, the position of the adiabat which represents the conditions in the accretion disk is not critical. The second reason comes from the range of applicability of thermochemical equilibrium: since reaction rates increase rapidly with temperature, where the disk is hot enough (that is, for short heliocentric distances), the equilibrium will be easily reached.

In his early model, Lewis had adopted an adiabat coming from the early preconception that the accretion disk should be very massive. Using Cameron's (1985) models C and D, which use only 0.74% and 0.23% of the Sun's mass for the fraction of the disk within 7 AU, I checked that the condensation sequence is not significantly changed, in spite of a much lower pressure everywhere. This verifies the statement of the previous paragraph.

The temperatures of planet formation implied by Lewis' model mean, of course, the temperatures at which the solid grains were removed from any further contact with the gas. From Weidenschilling's (1988) analysis, this is typically within a few thousand years of the sedimentation onset. For the Earth, this mean temperature seems to be very high on the adiabat describing some massive accretion disks, but it goes down to 900 K when the disk contains less than 1% of the Sun's mass. This average temperature corresponds to the exact position of the planet, and another term of ± 100 K must be taken into account for the width of the accretion zone of the future Earth. To improve this assessment of the Earth's formation temperature, other chemical clues must be developed.

Chemical Kinetics

When the temperature is not large enough, the thermochemical equilibrium may need extremely long durations to be reached. If the time available is too short, then chemical kinetics must be taken into account. Lewis *et al.* (1979) and Lewis and Prinn (1980) have thoroughly discussed the chemical kinetics in a gas mixture of solar composition. The largest time constants that turn out to be significant at 900 K are of the order of one century.

In particular, Lewis *et al.* (1979) have considered the carbon chemistry for the terrestrial planets, and they have been puzzled by their retention of carbon. In order to reach a sufficiently large carbon retention, they select an adiabat in the accretion disk that puts the Earth's zone near the peak of the thermodynamic activity of graphite. In spite of their efforts, they still find an amount of carbon two or three times *smaller* than the observed amounts on the Earth and on Venus.

For any adiabat, graphite activity goes through a maximum in the vicinity of the line separating the domains of CH_4 and CO (see Figure 4). Whatever the accretion disk model, bringing this maximum of graphite activity near the Earth's zone removes it from the vicinity of the asteroid belt, where it is needed to make the carbonaceous stuff of the carbonaceous chondrites. Modern adiabats, like those of Cameron's (1985) models C and D, bring the maximum of graphite activity near 2.6 AU.

Here we face again the need for a good cosmothermometer to settle the question of the unknown parameter in the accretion disk models. These models are consistent with the general scenario described by Lewis to explain the densities of the planets; but the formation temperature of the planets cannot be established accurately because of the ambiguities brought about later by the differentiation processes that have

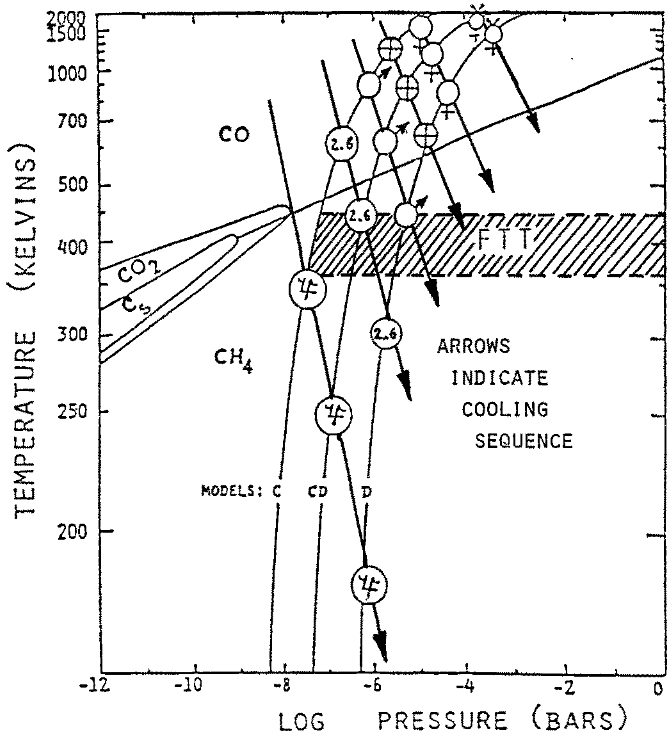

Fig. 4. Thermochemical equilibrium for carbon in a gas of solar composition. The quasi vertical curves are Cameron's 1985 adiabats. These adiabats can be interpreted as a cooling sequence. Adiabat CD brings the distance 2.6 AU at the high end of the FTT temperature zone, implying that dust sedimentation took place at that time. The same adiabat shows that, in the Earth's zone (symbol ⊕) *all* carbon was then in gaseous CO. The other lines separate the domains where more than 50% carbon is either in CO, or in CH_4 or in CO_2 or in C (graphite).

separated cores, mantles and crusts. All what we need is a single temperature devoid of the previous ambiguities. The temperature gradient of the accretion disk is sufficiently well understood to extrapolate this single temperature to the rest of the disk.

Accretion Temperature of the Chondrites

The central idea of this paper is that the most reliable information about the disk temperature, at the time of the dust separation from the nebular gas, can be found in the asteroid belt, from the undifferentiated parent bodies of the chondrites.

In particular, the separation of the dark C asteroids from the light S asteroids must be an effect of the temperature gradient in the dust grains, at the time of their accretion into larger objects. We interpret these objects as being the parent bodies of the (dark) carbonaceous chondrites, and of the (light) ordinary chondrites, respectively.

Since the C asteroids outnumber the S asteroids beyond 2.6 AU (Morrison, 1977), we interpret this distance as the place where we can define the best accretion temperature. It is true that the distribution of S asteroids extends beyond 2.6 AU, but their fraction falls off with an exponential scale length of about 0.5 AU (Zellner, 1979). The present distribution can be interpreted as resulting from the orbital diffusion through an originally much sharper limit near 2.6 AU.

The best cosmothermometer for the accretion temperature of chondritic meteorites probably is the fractionation of their volatile metals, Pb, Bi, Tl, In. Using the last three elements, Larimer (1967) and Anders (1971) found (for a nebular pressure of 10^{-4} bars) an average accretion temperature of 510 K for ordinary (L) chondrites, 450 K, 400 K and 340 K for C3, C2 and C1 carbonaceous chondrites respectively. These values should be all diminished by 30 to 60 degrees to take into account the lower pressures of the modern models of the accretion disk.

The state of oxidation given by the olivine-pyroxene ratio (Larimer 1968) gives temperatures varying from 500 to 700 K for the different types of ordinary chondrites, in agreement with the previous assessment. For the carbonaceous chondrites, the presence of FeS gives an upper limit of 680 K and the absence of magnetite Fe_3O_4 gives a lower limit of 400 K for most but not all carbonaceous chondrites.

The Fischer-Tropsch-Type (FTT) reactions, proposed by Anders (1971) and co-workers to explain the rich organic chemistry of the carbonaceous chondrites, would represent by far the best cosmothermometer because their grain catalysis would be pressure-independent. They would give 430 K for the C3, 400 K for the C2 and 370 K for the C1 chondrites, again in rather good agreement with the previous estimates.

The FTT reactions are those catalytic reactions that stop at metastable intermediates in the hydrogenation of CO (stable at high temperature) in CH_4 (stable at low temperature). The Fischer-Tropsch process was used in Germany during the Second World War to make gasoline from coke-oven gas (mostly $CO + H_2$).

It produced mostly straight-chain hydrocarbons in C_6, C_7, C_8, C_9 etc. by the hydrogenation of CO in the presence of fine magnetite grains supported by a porous matrix: a gel of hydrated silicates.

The FTT reactions generalize the Fischer Tropsch process to a gas of solar composition. Since N_2 is present at high temperature and NH_3 at low temperature, nitrogen also participates in the synthesis of a number of organic compounds including molecules that are important for living organisms, like amino-acids, purines and pyrimidines.

These organic compounds have been found in the carbonaceous chondrites, and Anders (1971) has assembled different arguments to demonstrate that they were due to FTT reactions. In particular the prevalence of straight chain hydrocarbons, the ^{13}C isotopic difference with carbonates, etc. Recent work has however established that this evidence is not unambiguous (Cronin *et al.*, 1988); also see Kerridge's (1992) discussion.

The chemistry of the carbonaceous material present in chondrites is a complex question that could not be covered thoroughly here, in particular because it is not directly relevant to the final conclusions. For more details see Prinn and Fegley (1989) or Cronin *et al.* (1988) where misgivings are discussed and the possible competition of the Miller-Urey synthesis is reviewed.

Exogenous Origin of Carbon and Water on the Earth

Since the temperature of the FTT reactions is not in disagreement with our other estimates, we have used them in Figure 4 for illustration purpose. However, if we choose to ignore the FTT reactions, it is important to remember that the other evidence still puts the temperature of 450 ±50 K at 2.6 AU at the time when dust was separated from the nebular gas. Using the *minimum* temperature of 400 K at 2.6 AU and using the slope of the adiabat of Figure 2, it is easy to see that the accretion temperature for the Earth was *at least* 1000 K, and possibly more.

This is also confirmed by using Cameron's (1985) adiabats C and D (Figure 4). The adiabat CD is the linear interpolation of the two previous adiabats. It is convenient because it brings the 2.6 AU distance exactly at the empirical temperature deduced before the separation of dust from gas. The adiabats are used for illustrative purpose and their accurate location is not essential. Although computed for three steady states, we can use them as an illustration of a cooling sequence.

As seen on Figure 4, the position of the Earth's zone, at the time of dust separation, is very high in the domain of CO. This means that the Earth is not going to accrete from chondritic dust, but from a dust very depleted of all volatile metals (Pb, Bi, In, Tl) and even somewhat depleted of Ag. There is no hydrated water in the silicates: water is entirely in the gas phase. Finally, all carbon is in gaseous CO, except possibly metastable carbon present in an aromatic polymer and brought into the accretion disk by incompletely processed interstellar grains. It is well known that ordinary chondrites still contain a small amount (typically 0.1%) of carbon in this form (Cronin *et al.*, 1988).

At that temperature, the iron grains were completely reduced, a prerequisite for them to sink eventually into the earth core. Let's remark that neither iron oxides nor silicates are dense enough to sink to the earth core, and cannot be reduced any more when imprisoned in the Earth's silicate mantle.

We come here to a first important conclusion: at this stage, the total amount of water present in our oceans, as well as the total amount of carbon (mostly present in the form of carbonates) must have an exogenous origin.

This can be extended to the terrestrial planets: if the 2.6 AU temperature can be trusted, we can use its gradient to establish the other temperatures. During the dust sedimentation to the mid-plane of the disk, the temperature was then close to 620 K in the zone of Mars, near 1200 K in the zone of Venus, and was kept near 1500 for Mercury, only because of the vaporization of the silicates.

These rather high temperatures imply that, just before its accretion into planetesimals, all dust was outgassed. All carbon, all water and most labile elements were missing or very depleted in the dust that made the terrestrial planets.

The origin of all volatile elements on the terrestrial planets would then be quite mysterious, if it were not explained in a straightforward manner by the inevitable orbital evolution taking place during the final phases of planetary accretion. The phenomenon that is going to change the nature of planetesimal accretion, is the growing gravity of the first planetary embryos. This gravity is not only going to produce a runaway growth of the largest bodies, but it is going to produce an orbital diffusion. In particular, the growth of the giant planets is going to send bodies with volatile ices to the zones of the terrestrial planets. These bodies are first, chondrites of the different types and later on, icy planetesimals volatile enough to be called comets.

Orbital Diffusion

Let's consider the phenomenon of orbital diffusion in more detail. At a steady state between velocity damping by inelastic collisions, and velocity increase by grazing passages, Safronov (1969) finds that the *mean* relative velocities in the swarm of smaller bodies grow in proportion to the escape velocity of the *largest* body in the swarm. Since the largest body grows steadily by accreting smaller bodies, the growth of the *mean* relative velocity produces orbital changes that enlarge the mean eccentricity of the orbits. Therefore, the zone swept by the minor bodies is also enlarged.

This effect is particularly important for the giant planets because of their large escape velocity, which allows a considerable diffusion of their icy planetesimals (= comets) into the zones of the terrestrial planets. The present orbital diffusion of the short-period comets by the giant planets is another example of the same rules of the game.

This is not the place to review the difficult question of Jupiter's formation. However, Wetherill and Chapman (1988) have shown that a runaway growth of a Jupiter's core of several Earth masses is possible in half a million years. This seems to happen just in time for a massive Jupiter to be able to stop the formation of a planet in the asteroid belt. The early existence of a massive proto-Jupiter is the only mechanism that has been proposed to scatter the mean relative velocities of the swarm of asteroids and prevent the formation of a large planet. For this reason, the absence of a planet at 2.8 AU is a reasonable argument that a massive Jupiter existed after only a few million years.

In the outer solar system, the accretion times needed to build a planet, grow roughly in proportion to the orbital periods around the Sun. Hence it is understandable that the terrestrial planets had already reached 90–95% of their masses, before a substantial number of icy planetesimals were deflected enough by Jupiter to reach the zones of the terrestrial planets. It is possible to estimate the mass of volatile planetesimals, accreted onto the terrestrial planets by orbital diffusion. I proposed a model for this purpose (Delsemme 1981, 1984). The model is rather easy to compute because the mass of the giant planets is known and Safronov has given a theory providing the scattered masses as a function of the planetary masses. The major contribution clearly comes from Jupiter. Saturn contributes 20% of the total mass, whereas the contribution of Uranus and Neptune is negligible.

More recently, new evaluations have confirmed my analysis, although they go somewhat beyond my results. Matsui and Abe (1986) find that comets brought down to Earth four times as much water as the mass of our oceans. Fernandez and Ip (1981, 1983) have revised Safronov's evaluations and found that the mass perturbed towards the orbits of the terrestrial planets is more than an order of magnitude larger than Safronov's figures. Ip and Fernandez (1988) find now that ten times the present mass of our oceans has been brought down to Earth by comets. Chyba (1987) uses the visible craters of the Moon to estimate the latest bombardment. He finds that the total mass of our oceans corresponds to a bombardment of only 10% of the lunar craters. Owen *et al.* (1991) have found evidence for cometary impacts in the noble gases of terrestrial planets.

My model (Delsemme, 1991) was based on Safronov's (1972) analytical approach that he developed to deduce the mass of the Oort Cloud, from the ejection of bodies by the giant planets. Using all his assumptions, I had neglected all ejections of planetesimals due to distant encounters and resonances. Although difficult to estimate, these ejections multiply the total mass shed to the Earth by a factor larger than two but smaller than five. In my new results displayed in Table I, I have now used my best estimate of 3.5 for this factor; I have also added the contributions from the zones of Uranus and Neptune, that have become less negligible than before.

The chondrites from the asteroid zone represent a weighted average for all chondrites, including ordinary and carbonaceous chondrites. This means that they are assumed to contain 0.3% water and 0.3% carbon. In the model, a density of 1 is used for water, 2 for carbon and 3 for silicates. The distribution of silicate,

TABLE I

The exogenous origin of water,carbon and volatiles on the earth

Origin of bodies	Mass shed to Earth's zone	Thickness of uniform layer on the earth			
		Stony	Water	Carbon	Gases
Chondrites from asteroids' zone	3 M_0	2 km	20 m	10 m	—
Comets from Jupiter's zone	13 M_0	3 km	11 km	4 km	600 bars
Comets from Saturn's zone	3 M_0	1 km	3 km	1 km	140 bars
Comets from Uranus' zone	0.5 M_0	150 m	500 m	150 m	23 bars
Comets from Neptune's zone	0.2 M_0	60 m	200 m	60 m	10 bars
Totals	19.7 M_0	6 km	15 km	5 km	733 bars
Masses in 10^{21} kg:		9.0	7.5	1.0	0.7

M_0 represents the mass of the Earth. The missing mass in the asteroid's zone is assumed to be 10 M_0. The present oceans would make a uniform layer of 2.6 km on the Earth.

water, organics and gases is based on data from Halley's comet (Delsemme 1991) namely, by mass, 43% water, 26% organics and 31% inorganics (labelled stony in Table I).

Discussion

Since the two ideas developed in this paper are independent from each other, they will be discussed separately.

1. Before accretion, the early particles were fine, hot and degassed

The empirical evidence of a dust sedimentation that took place 4.55 billion years ago, is found in chondrites, those primitive meteorites that came from the asteroid belt. The radiometric age of a very large number of chondrites is surprisingly exactly the same. Chondrites are aggregates of very fine grains in different oxidation states, different volatilities, hence different origins.

Before planetary formation, there was an accretion disk surrounding the Sun. This disk kept dust in suspension by violent turbulence in the gas. As soon as turbulence subsided, dust sedimented to the mid-plane of the disk, forming very fine rings surrounding the Sun. In the rings, dust accreted into larger and larger bodies, fast forming numberless bodies in the 1 to 10 km size range: the planetesimals.

In the planets, igneous processes have completely erased any trace of the primeval grains, but we recognize them in the chondrites and identify their aggregation process as the one that started by the sedimentation of dust from the gas of the solar nebula. For this reason, we have very little doubt that the dust particles that formed the Earth were fine grains of silicate and of reduced iron that separated from a gas of solar composition (mostly hydrogen). Their temperature during this separation was however in doubt because they were processed by heat later. The first idea developed here is a way to assess this temperature.

In the solar nebula, the temperature varies approximately with the inverse of the distance r to the Sun. This is widely model-independent with two conditions; first, the gravitational potential must also be in $1/r$ (this happens as soon as the mass of the protosun prevails at the center); second, there must not be any catastrophic change in the moment of inertia of the disk (this is always true during the accretion of the planets). Then, the temperature distribution is a direct consequence of the shape of the gravitational potential, combined with the virial theorem.

Let's also note that the adiabatic assumption is used in most models of the solar nebula, because convection is much more effective than any other mode of heat transport in the temperature range of the Solar Nebula. The adiabat sets the pressure in the gas, as soon as the temperature is known, but the assumption is not critical for our discussion.

To find the temperature of the Earth's dust before its accretion, the real problem is to find a good cosmothermometer not too far away from the Earth, and to extrapolate to the Earth with the temperature gradient in $1/r$ of the nebula. We have shown that the best known cosmothermometer is located at 2.6 AU: a temperature of 450 K separates the formation of carbonaceous chondrites from that of ordinary chondrites. The straight extrapolation with the $1/r$ gradient gives then 1170 K at the Earth's distance.

It is difficult to escape from the conclusion that the dust temperature in the Earth's zone was larger than 1000 K when it separated from the nebular gas. Considering chemical kinetics, we also come to the conclusion that the dust was at chemical equilibrium with gas at that temperature. This implies that all carbon was in CO in the gas phase with a large excess of H_2, and all water was also in the gas phase as steam. Iron grains were completely reduced, and silicate grains were degassed and depleted in labile elements.

This leaves us with the problem of a late, exogenous origin of carbon, water and labile elements, that is addressed in the second part of this paper.

2. Later, orbital diffusion of comets brought a volatile veneer onto the Earth

The planetesimals formed by agglomeration of dust in the solar nebula, were stony within 2.6 AU, carbonaceous from 2.6 to about 4 AU, and were icy bodies, that is comets, beyond 4 AU. This is implied by the temperature gradient in the nebula and confirmed by observations of bodies in the outer Solar System.

The embryos of the giant planets (from 5 to 30 AU) were therefore formed by comets, about at the same time when the Earth was formed. The reason is that the sedimentation of solid grains took place almost simultaneously everywhere, because it was due to the end of the gravitational collapse of the interstellar cloud that was feeding turbulence in the gas. The only difference is that the dusty grains were frosty because of the lower temperature, hence they formed comets instead of stony planetesimals.

The gravitational collapse of the *gas* of the nebula is required to explain the total mass and the composition of Jupiter and Saturn. However, it has been established that this collapse cannot occur before the planetary embryo becomes larger than about 10 Earth masses (Mizuno, 1980). This is a universal result which does not depend on the pressure, temperature or location in the solar nebula.

Safronov (1972) has shown that, as the embryos become larger, their growing gravity becomes large enough to produce the orbital diffusion of billions of icy planetesimals. The total mass of the scattered bodies is directly related to the total mass of the embryos. A large fraction is ejected out of the Solar System, another fraction is stored in a 50 000 AU sphere surrounding the Solar System (a likely origin of the Oort cloud). Since this scattering is a random process, a fraction of the scattered bodies is ejected to the inner Solar System.

Using Safronov's analytical approach, I have computed the total mass shed to the Earth's zone, multiplied by the collision probability with the Earth. The results of Table I were found under the same assumptions as Safronov's, that the masses of the giant planet's embryos were in the range of 10 to 20 terrestrial masses; namely, 9 for Jupiter, 12 for Saturn, 14 for Uranus and 17 for Neptune. A factor of 3.5 was used to correct for the far encounters and resonances that are neglected by Safronov's theory (this correction was not yet done in Delsemme, 1991).

A more recent analysis of the rock, iron and C, N, O content of the giant planets (Hubbard, 1984) yields 15 terrestrial masses for Jupiter's embryo, and 19 for Saturn's. This assumption would multiply the results of Table I by a factor of 1.7 for Jupiter and 1.6 for Saturn. It is interesting to underline that the model depends only on the *total* mass of the embryos and predicts the *total* mass scattered; in particular it is independent of the number and of the size distribution of the comets scattered.

How does the model compare with observational evidence? The craters on the Moon show the scars left by the impacts that followed its solidification. This leaves a long period which is unaccounted for, usually assumed to be about 150 million years. Gravitationally scaling to the Earth, Chyba (1991) finds that 1.5×10^{22} kg of material accumulated on the Earth *after* the first 150 million years. This raises the question of the time scales for the events summarized by Table I.

Safronov's analysis shows that the characteristic times for orbital scattering grow with the orbital period of the planet involved. Calling t the time scale for diffusion (that is, the time needed for the number of scattered bodies to decrease by a factor 1/e), I find the following results:

Zone:	Asteroids	Jupiter	Saturn	Uranus	Neptune
t in million years	25	60	150	400	800

If the scattering of comets predates the completion of the Earth's accretion, it could be argued that a large fraction of the comets contributed more to the mantle and the core of the Earth than to the crustal veneer.

However, we know that the sedimentation of solid grains to the mid-plane of the nebula occurred almost simultaneously everywhere, because it is due to the same cause: the end of the gravitational collapse of the interstellar cloud that was providing the energy for the turbulent motions in the gas.

If the Earth's accretion took about 100 million years (Wetherill 1980, Stevenson 1983) then the embryos' accretion took at least as long, probably longer because the orbital periods are much longer, and large embryos' masses were already needed for the first comets to be deflected enough to reach the Earth. Hence we can safely assume that the accretion of the Earth took place in two well separated waves. The first wave lasted 100 million years and accreted 99.999% of the Earth's mass with degassed silicates and iron particles. The second wave started at the earliest some 150 or 200 million years later than the first wave, and lasted 500 or 600 000 years. It brought water and carbon compounds from the zones of the giant planets and also siderophiles at the surface of the Earth, after they had been depleted in the crust by the previous differentiation of the Earth. Chyba (1991) has addressed quantitatively the question of the 'excess' siderophiles.

In spite of the uncertainties inherent to my model and to Chyba's (1991) estimates, the good coincidence between Chyba's value (1.5×10^{22} kg) and my Table I (its totals turn out to be 1.8×10^{22} kg) can be construed as supporting the previous interpretation. Linear cratering rates have subsided considerably after some 600 million years (Weissman 1989) but cratering went on. In a sense, the 100-odd short period comets are all on unstable orbits that will eventually bring them in collision with the terrestrial planets. Since their source is the Kuiper belt, from where they are scattered by resonances with the giant planets, one can say that the process never stopped and is still going on for those orbits that have an extremely long time scale for diffusion.

Interestingly, Hartmann (1987, 1990) has argued that there is direct solar system evidence for an early intense scattering of C-type objects by Jupiter, which establishes some possible direct evidence for the mechanism we use in the asteroid belt. Of course, the best signature of such a mechanism probably remains the Kirkwood gaps, where the depletions coincide exactly with resonances from the orbital period of Jupiter.

The thickness found for the more volatile veneer is of the same order of magnitude as the mean thickness of the Earth's crust (14 km) but there is no possible identification, because the crust has been recycled many times in the outer mantle. The rocky fraction of the veneer diffused into the upper mantle, explaining the present distribution of the volatile elements and labile compounds.

Our model explains why there is an excess of siderophile elements in the upper mantle, as shown by the chondritic values of the ratio nickel to cobalt, iridium to gold, osmium to palladium (Morgan *et al.*, 1981). Jacobson and Wasserburg (1984) conclude the same for the isotopes of neodymium. This matter has been quantified by Chyba (1991). Finally, the original dust is highly reduced and volatile-poor, whereas the chondritic-cometary contribution is very oxidized and volatile rich. This mixture is requested by pure chemical arguments.

In particular, Ringwood (1979) and Wänke (1980) as well as Wänke and Dreibus (1988) have already proposed a two component model. Anders and Owen (1977) and Morgan and Anders (1980) have also developed models based on the mixing of a chondritic component with something else. These models were developed on the basis of purely chemical arguments without identifying the mechanisms that could bring volatile components onto the Earth. The present paper has described the necessary and inevitable mechanism that is going to bring a chondritic/cometary component, highly oxidized and volatile, as a veneer to the terrestrial planets.

Conclusion

The present model gives a solution to two major problems in geophysics, namely the existence of 'excess volatiles' and of 'excess siderophiles' on the Earth. The 'excess volatiles' are not only the atmosphere and the oceans, but also the carbon present in the carbonates and living organisms, as well as an excess of other volatile elements and labile compounds.

The 'excess siderophiles' are found in chondritic (or solar) proportions, at least in some rocks of the crust and the upper mantle. Siderophile elements, by definition, have an affinity for metallic iron, and the formation of the metallic core should have diminished their proportions elsewhere, at least if they were already on the Earth when the core was formed.

The exogenous origin of the 'excess volatiles' and of the 'excess siderophiles' on the terrestrial planets does not require any ad hoc hypothesis. It derives of necessity from the formation mechanisms of the planets by planetesimals. Collisions between planetesimals are soft at first because orbits are coplanar and quasi-circular. The nature of the process changes only when the largest bodies develop a significant self-gravity. This has two consequences: a runaway growth of the largest bodies (that are going to become the planets) and an orbital diffusion of the smaller ones.

Only the latter process is of consequence for our purpose: the growth of Jupiter and Saturn is going to deflect numberless chondritic asteroids and comets across the inner solar system. The bombardment of the terrestrial planets by these objects is going to bring the right amount of 'excess volatiles' and 'excess siderophiles' to the Earth's crust. The subsequent recycling of the crust into the upper mantle will produce a diffusion of the siderophile elements and labile compounds, whereas the major fraction of the oceans and even more of the atmosphere will be lost in the final collisions of the accretion process.

Going backwards in time, another proof of the necessity of the previous processes is found in the temperature of the accretion disk at the time when the metallic and silicate dust that was going to form the Earth, was separated from the gas phase of the nebula. Models of the viscous accretion disk do not provide this temperature without some ambiguity, but they provide a reliable temperature gradient. The best way to standardize the temperature is to use bodies that have not been differentiated by a large gravity. The best bodies are the parent bodies of the chondrites.

A temperature of more than 1000 K is deduced at the time when the dust going to form the Earth was separated from the gas phase. This implies grains of anhydrous silicates and of reduced iron, without either any water, or any carbon or any labile elements. The only possible exception could be metastable polymers preserved from interstellar grains, like polyaromatic hydrocarbons (PAH). The paradigm describing the origin of the solar system does require an exogenous origin of water and carbon on the Earth, but it also provides the mechanism to do so.

The present model brings the right amount of siderophiles in silicates, but six times more water and 700 times more gases than what remains now on the Earth. Considerable losses of volatiles are expected because of giant impacts with already large protoplanets, during the final phases of the accretion of the terrestrial planets. These giant impacts are predicted by theory (Wetherill, 1991) and one of them is probably responsible for the formation of the Moon, but because of the stochastic nature of the process, atmospheric and oceanic losses have not been reconstructed quantitatively.

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