IS EXTRATERRESTRIAL ORGANIC MATTER RELEVANT TO THE ORIGIN OF LIFE ON EARTH?

D. C. B. WHITTET
Department of Physics, Applied Physics and Astronomy, Rensselaer Polytechnic Institute, Troy, NY 12180, U.S.A.

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Abstract. I review the relative importance of internal and external sources of prebiotic molecules on Earth at the time of life's origin ~3.7 Gyr ago. The efficiency of synthesis in the Earth's atmosphere was critically dependent on its oxidation state. If the early atmosphere was non-reducing and CO_2-dominated, external delivery might have been the dominant source. Interplanetary dust grains and micrometeorites currently deliver carbonaceous matter to the Earth's surface at a rate of $\sim 3 \times 10^5$ kg/yr (equivalent to a biomass in ~2 Gyr), but this may have been as high as 5×10^7 kg/yr (a biomass in only ~10 Myr) during the epoch of late bombardment. Much of the incoming material is in the form of chemically inactive kerogens and amorphous carbon; but if the Earth once had a dense (~10-bar) atmosphere, small comets rich in a variety of prebiotic molecules may have been sufficiently air-braked to land non-destructively. Lingering uncertainties regarding the impact history of the Earth and the density and composition of its early atmosphere limit our ability to draw firm conclusions.

1. Introduction

In at least one sense, a connection between the Universe at large and life in our small corner of it is inevitable. The hydrogen, carbon, nitrogen, oxygen, and other elements that make up our bodies and other living things were created billions of years ago in the interiors of stars and, in the case of hydrogen, in the the Big Bang itself (see Trimble, 1997, in this volume for an eloquent review). That our atoms are the product of cosmic physics is established; it is much less clear that our molecules are in any sense the product of cosmic chemistry (or biology).

Interstellar space might, indeed, seem an unpromising location for significant chemical evolution. By terrestrial standards, it is an almost perfect vacuum: even in relatively 'dense' clouds, densities are typically a factor $\sim 10^{15}$ less than in the Earth's atmosphere at sea level. Low temperatures and densities dictate that only exothermic reactions generally proceed at any reasonable rate. Even the timescales available are not particularly favorable – the typical lifetime of a molecular cloud, $\sim$ 10–100 Myr, is short compared with timescales available on an earthlike planet orbiting a sunlike star. However, one major advantage is that the chemical environment in interstellar clouds is overwhelmingly reducing.

Many previous papers in this volume have discussed or alluded to the production of significant prebiotic organic molecules in the interstellar medium and/or the protosolar nebula that gave birth to the Sun and planets. Evidence for the presence

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of organics in interstellar gas and dust is compelling, and support for the hypothesis that interstellar material survived the origin of the solar system to become incorporated into planetesimals is growing as we learn more about the nature of comets and asteroids. Organic molecules may also be synthesized by processes occurring in the solar nebula itself. Proof that the cosmos currently delivers at least *some* exogenous organic molecules, including amino acids, onto the surface of the Earth is provided by analysis of carbonaceous meteorites. In this paper, I attempt to review the current arguments for and against a major contribution by such materials to the reservoir of prebiotic organic molecules available on Earth at the time of life's origin. Although no final answer is yet possible, key factors which determine the outcome can be clearly identified.

2. Timescales and Scenarios for the Origin of Life

Astronomy, geology and paleontology combine to delimit the epoch of the origin of life on Earth. It is generally agreed that the solar nebula condensed from an interstellar cloud some 4.57 Gyr ago, and that the Earth formed almost simultaneously by coagulation and accretion of planetesimals (e.g. Tscharnuter and Boss, 1993; Harper, 1996; Gaffey, 1997, and references therein). After initial accretion, the Earth was hot and largely molten. The primitive atmosphere was rich in water vapor which condensed into oceans as soon as the surface cooled sufficiently. Once surface water existed, the Earth was in principle habitable by primitive life. However, bombardment by asteroidal-sized bodies appears to have continued for several hundred Myr after the initial accretion phase that formed the Earth and other planets. A large comet or asteroid, greater than $\sim$ 50 km in diameter, could supply enough energy to boil the oceans and destroy life (Maher and Stevenson, 1988; Sleep *et al.*, 1989; see Figure 1). If the lunar cratering record is a reliable pointer to the early impact history of Earth (Section 3), then we may deduce that these sterilizing impacts continued up to about 3.8 Gyr ago. At this point, the mean free time between such impacts became large compared with the age of the Earth, although lesser impacts may have been responsible for mass extinctions of species in more recent times (Alvarez *et al.*, 1980; Rampino and Haggerty, 1994).

The earliest direct evidence for life is provided by the oldest microfossils, which date from $\sim$ 3.5 Gyr ago (Schopf, 1992, 1993). The organisms they represent (primitive cyanobacteria) may have taken a considerable time, perhaps as long as a few hundred Myr, to evolve to the stage of complexity found in the samples. The oldest fossils are comparable in age with the oldest crustal rocks and sediments, indicating that these studies are likely to be sample-limited. Carbonaceous inclusions of possible biotic origin were recently reported in 3.8 Gyr-old sediments by Mojzsis *et al*. (1996). We conclude that microbial life was established 3.5 Gyr ago, and may well have been present for some time.

Indirect evidence for early life is provided by the geological record. Banded

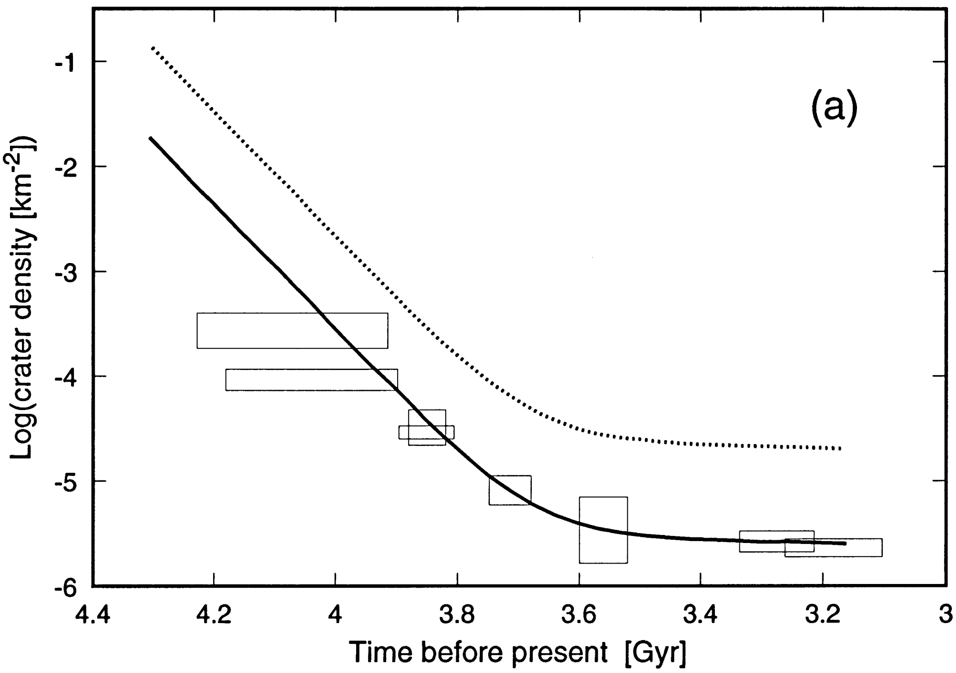

Figure 1a–b. Cratering history and impact frustration of early life. (a) Cratering history as a function of surface age for the Moon (solid curve) and Earth (dotted curve). Crater density is the number of craters greater than 20 km in diameter per km^2. Open boxes represent data from lunar crater counts associated with Apollo landing sites (Carr *et al.*, 1984). Earth bombardment is assumed to be higher than that of the Moon due to gravitational focusing and differing impact speeds and surface gravities (Maher and Stevenson, 1989). (b) Interval between major Earth impact events as a function of time, as calculated by Maher and Stevenson (1989). Lower curve: impact sufficient to cause global surface trauma and climatic change (as postulated for the K/T event). Middle curve: impact sufficient to cause global surface sterilization (SS). Upper curve: impact sufficient to boil the oceans and cause total sterilization of the planet (TS).

iron formations (BIFS), composed of alternating layers of iron-rich and iron-poor sedimentary rock, are taken as evidence of the presence of free oxygen in the atmosphere (Schopf, 1992). The oxidized iron minerals found in the iron-rich layers are formed when iron dust, released to the atmosphere by volcanic activity, combines with molecular oxygen in the upper stratum of the oceans; the resulting iron oxides are insoluble in water and consequently settle to the ocean floor, forming the BIFS. The atmosphere must have been at least weakly aerobic for this to occur, and the primary source of atmospheric O_2 is photosynthesis (Kasting, 1997). The earliest BIFS date back to 3.5–3.8 Gyr, suggesting that organisms capable of oxygenic photosynthesis already existed at this time.

Taking all known constraints into consideration, the best current estimate for the epoch of the origin of life is 3.7 ± 0.2 Gyr before present. However, it is safest to treat this result as a lower limit: it seems unlikely that future research will lead to a

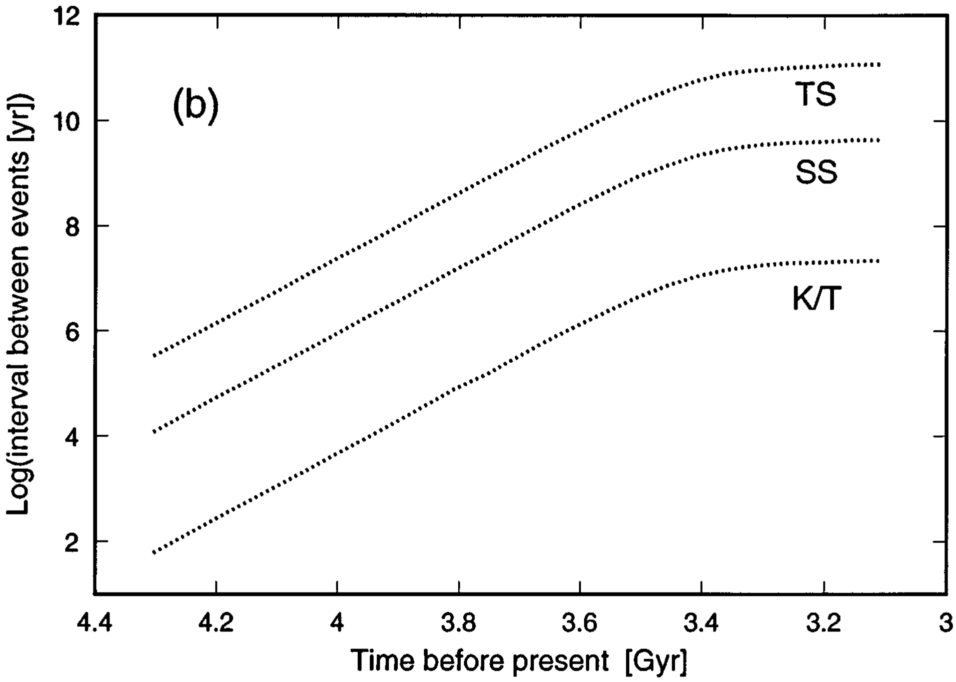

Figure 1b.

significant downward revision, whereas an upward revision (towards earlier times) is not inconceivable, e.g. if older fossils are discovered, or if the impact sterilization constraint is alleviated by a different interpretation of the cratering record. In any case, life appears to have become established quite soon after conditions rendered it viable.

Several scenarios are proposed for the origin of life on Earth and the reservoir of organic compounds from which it emerged. These may be summarized as follows.

Scenario [1]: The entire process was intrinsic to the Earth. As a starting point, amino acids and other important prebiotic molecules were produced by reactions occurring in a reducing (hydrogen-rich) atmosphere, energetically driven by phenomena such as electric discharge or solar ultraviolet irradiation (Miller, 1992; Clarke and Ferris, 1997; see Section 4). Reactions driven by geothermal energy in submarine hydrothermal systems may also have provided a major source of prebiotics (Baross and Hoffman, 1985), with the added benefit of relative immunity to destruction by all but the most catastrophic impacts. Prebiotics ultimately evolved into nucleic acids (‘RNA world’) and then life.

Scenario [2]: Infusion of extraterrestrial material played a significant or dominant role in providing the reservoir of organics, either by delivery of key prebiotic molecules formed beyond the Earth, or by impact shock-driven synthesis in the atmosphere (Anders, 1989; Chyba, 1990; Chyba *et al.*, 1990; Chyba and

Sagan, 1992). Prebiotics supplied in this way included HCN, H_2CO, and possibly NH_2CH_2COOH (glycine) and other amino acids. Delivery at some level is known to occur now, and seems very likely to have occurred then, perhaps at a much higher rate; the central issue is how this source of prebiotics compares in terms of quality and quantity with indigenous sources. We return to this problem in Section 5.

Scenario [3]: Cosmic delivery of pre-existing organisms seeded the Earth with life (‘panspermia’). This proposal, first discussed by Arrhenius (1903), has reappeared in a number of forms (e.g. Hoyle and Wickramasinghe, 1979; Crick, 1981). Delivery might be via random accretion of life-bearing meteorites or cometary dust, deliberate introduction by extraterrestrial intelligence (‘directed panspermia’; Crick, 1981), or even accidental ‘contamination’ by passing space travelers. Of course, to invoke an external source of life on Earth does not solve the problem of its origin but merely displaces it.

Davies (1988) describes panspermia as ‘Unlikely, unsupported but just possible’. There is no *a priori* objection to the concept of interstellar organisms (Sagan, 1973) but the densities prevailing in molecular clouds are insufficient to allow appreciable evolution within cloud lifetimes, and organisms exposed to the harsh radiation field permeating regions outside of molecular clouds are rapidly destroyed by ultraviolet irradiation (Weber and Greenberg, 1985). If biological organisms exist in non-planetary environments, the most viable location is probably comets. However, comets merely provide a possible means of cold storage and transport, not a medium for formation and growth. Excitement has been generated by the recent possible detection of microbial fossils in a meteorite originating from Mars (McKay *et al.*, 1996; see McKay, 1997, in this volume). If confirmed, this will be a momentous discovery; but implications in terms of panspermia are limited to the possibility that life originating in the putative Martian biosphere might have been delivered to Earth (or conversely; see Melosh, 1988). No credible evidence has yet been presented for the existence of extraterrestrial organisms of wider provenance, either within or beyond the solar system. Lacking such evidence, I limit the scope of this review to the question of whether the cosmos provided the molecular building blocks of life, rather than life itself.

I conclude this section with another caveat. How prebiotic molecules evolved from whatever brand of primordial soup one prefers into the first replicating organisms is, of course, the million dollar question: mercifully, it is beyond the astronomers’ brief (and the scope of this review). For discussion of current issues, see Chyba and McDonald (1995) and references therein.

3. The Impact History of the Earth-Moon System

Ancient surfaces throughout the solar system bear the scars of bombardment by comets and asteroids. The Earth is unusual in having relatively few impact craters, the ancient record having been erased by tectonic plate movement, volcanism and erosion. Crater-forming bodies of diameter $d > 1$ km undergo little deceleration in the atmosphere and strike the surface at essentially their cosmic speed of 10–30 km/s. As noted in the previous section, bombardment by substantial ($d > 50$ km) bodies would have presented a formidable barrier to the origin and sustainability of life on Earth. However, much smaller particles such as dust grains and small meteorites are decelerated to terminal speeds of only a few m/s (Anders, 1989) and may suffer little or no ablation. It is clearly important to know the input flux of objects in both of these contrasting size domains during the first Gyr of Earth's history.

Current models for the flux of impactors as a function of time are based on the interpretation of crater populations on the Moon. The Moon is generally agreed to possess a geological memory of $>$3.5 Gyr events that is vastly superior to that of the Earth. Crater density counts provide the principal basis for current flux models (e.g. Figure 1a), yet laboratory analyses of lunar samples appear to contradict the hypothesis of a steady decline in impact flux through time. A sharp cut-off is found at about 4.0 Gyr in the ages of impact-generated melt rocks collected at the six Apollo landing sites. One interpretation of this is that the Moon (and Earth?) experienced a 'terminal cataclysm' during a 100 Myr interval between 3.85–3.95 Gyr that generated most of the large ($>$30 km) craters currently observed on the Moon (Tera *et al.*, 1974; Ryder, 1990). According to Ryder (1990), the Moon was heavily bombarded during the accretion phase, up to about 4.4 Gyr ago, and then, after a period of quiescence, experienced a spike in the flux at about 3.9 Gyr. This interpretation requires that there were at least two distinct populations of space debris, as it seems unlikely that a swarm of planetesimals from the early accretion phase could be of stored for $\sim$600 Myr (Wetherill, 1975). Ryder (1990) speculates that the terminal cataclysm about 3.9 Gyr ago may have been caused by collision of two additional Earth-orbiting satellites that generated a short-lived population of debris within the Earth/Moon system.

If we assume that the intense lunar bombardment that occurred 3.9 Gyr ago was also inflicted on the Earth, then it would presumably have been sufficient to cause global sterilization (whatever its origin); in this case, the impact constraint on the epoch of life's origin (Section 2) remains in place. A more difficult question concerns the flux history of smaller meteorites and interplanetary dust particles supposed to have delivered unablated organic matter. There is some evidence from studies of the micrometeorite component of ancient terrestrial sediments and lunar regolith that the arrival rate has remained roughly constant for the past $\sim$3.6 Gyr (see Chyba and Sagan, 1992, for a review). What happened before this? Was the accretion rate of diffuse matter closely correlated with that of the crater-forming bodies, or had it already decayed to something approaching its current level by 3.9 Gyr? If late bombardment was a solar-system-wide phenomenon, then the complete spectrum of particle sizes and compositions would likely have been involved. In this case, the accretion rate of carbonaceous material could have been a factor of 100 or more higher than it is today. But if late bombardment was caused by some local catastrophe, possibly involving breakup of one or more bodies of lunar dimensions and composition, it may have delivered no additional organics to Earth at all.

4. Endogenous Production

Miller was the first to successfully synthesize prebiotic compounds, including amino acids, in the laboratory by simulating conditions on the primitive Earth (Miller, 1953; Miller and Urey, 1959). In the original form of this classic experiment, an electric discharge provided the energy source driving reactions in a reducing atmosphere composed of H_2, H_2O, NH_3 and CH_4. Prebiotics are formed by solution reactions between molecules such as HCN and H_2CO, produced directly in the discharge from the atmospheric gases and their dissociation products (see Miller, 1992, for a more recent account of this work). One of the most striking results of the experiment was the finding that the molecules formed are not a random mixture of organic compounds; a relatively small number are produced in substantial yield, and these are, with few exceptions, of biological significance. The yield of such molecules can be quite high; for example, glycine alone may account for as much as 2% of all carbon in the products.

Subsequent variations of the original Miller-Urey experiment were designed to investigate the sensitivity of the yield to initial assumptions, in particular, the composition of the atmosphere (Schlesinger and Miller, 1983a,b; Miller, 1992). Rather than CH_4 and NH_3, current models (Section 6) favor CO_2 and N_2 as the primary carriers of carbon and nitrogen. Whereas CH_4 and NH_3 are relatively easily dissociated into radicals, CO_2 and N_2 are more stable. NH_3 would have tended to dissolve in the primitive oceans and might not have been abundant even in a reducing atmosphere. However, substitution of N_2 for NH_3 is less critical than substitution of CO_2 for CH_4. The limiting step appears to be the production of HCN (Kasting, 1993, and references therein), which requires initial dissociation of both CO_2 and N_2 in a non-reducing atmosphere. Both C=O and N≡N bonds can be severed in a lightning discharge, but the resulting C and N atoms are more likely to combine with oxygen than with each other or with hydrogen in a non-reducing atmosphere.

Figure 2 compares amino acid yields for an atmosphere of H_2, H_2O, N_2 and either CH_4 or CO_2 (Miller, 1992). Results are displayed as a function of the H_2 concentration. Lack of free H_2 is no barrier to organic synthesis in an atmosphere with CH_4 as the carbon source. But when CH_4 is replaced by CO_2, the yield falls rapidly as the H_2/CO_2 ratio falls below unity. Although Figure 2 is based on electric discharge experiments, the trend towards low yields in non-reducing atmospheres is a general result, not critically dependent on the energy source driving the reactions

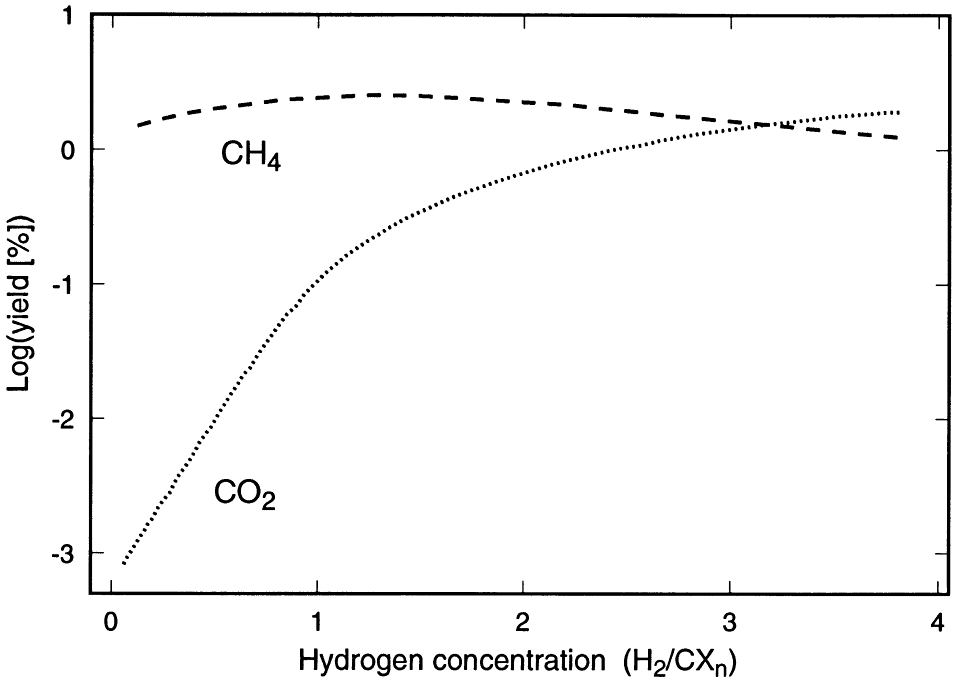

Figure 2. Results of the Miller-Urey experiment displayed as percentage amino acid yield versus initial hydrogen concentration H_2/CX_n, where CX_n represents either CH_4 (dashed curve) or CO_2 (dotted curve). In each case, the experiment was performed at room temperature in an atmosphere containing equal partial pressures of N_2 and CX_n together with H_2. At low H_2 concentration, the yield is two to three orders of magnitude lower when the initial carbon carrier is CO_2. (Adapted from Miller, 1992).

(see Chyba and Sagan, 1992, for a review). An atmosphere that was at least mildly reducing would appear to have been a prerequisite if efficient prebiotic synthesis in the primitive Earth environment was important to the origin of life.

Chyba and Sagan (1992) estimate the total production rate, $\dot{m}$, of organics by various endogenous processes, including electric discharge, coronal discharge, photochemical reactions and shocks*. Results are presented for 'standard' reducing and non-reducing atmospheres; in either case, UV photochemical reactions are the primary source of organics in the models. In the reducing atmosphere, $\dot{m} \sim 2 \times 10^{11}$ kg/yr. In the non-reducing atmosphere adopted by Chyba and Sagan (which contains H_2 as a minor constituent at a concentration of $H_2/CO_2 = 0.1$), $\dot{m}$ is approximately three orders of magnitude smaller. Lower H_2 concentrations will naturally lead to even lower production rates. We compare these results with exogenous delivery rates in the following section.

* Included here are organics synthesized by meteoritic impact shocks, in which the importance of the projectile is limited to providing the energy source driving chemical reactions.

5. Exogenous Delivery

Organic molecules in exogenous material accreting onto the Earth's surface will not survive impacts at speeds above about 10 km/s (Chyba *et al.*, 1990), and this precludes delivery by bodies greater than about 50 m in radius if we assume present-day atmospheric density and pressure. Projectiles that might deliver organic molecules intact to the surface take two distinct forms, meteorites (especially carbonaceous chondrites) and interplanetary dust, the parent bodies of which are believed to be C-type asteroids and comets, respectively. It is now well-known that carbonaceous chondrites contain prebiotic molecules, including small but significant quantities of amino acids (Kvenvolden *et al.*, 1970; Kerridge, 1989). Their extraterrestrial origin is established on the basis of diversity, molecular structure and isotopic composition. The chondrites contain a much wider variety of amino acids than is normally found in terrestrial organisms, and their structure is racemic, suggesting abiotic synthesis (Chyba, 1990). The amino acids share the deuterium enrichment found in other meteoritic organic extracts, such as kerogen, and this strongly hints at synthesis by processes operating in the interstellar medium or the solar nebula (Tielens, 1983; Kerridge, 1989) rather than in a planetary environment.

Although carbonaceous chondrites are known bearers of exogenous organics, their contribution, at least in terms of mass, is small compared with that of interplanetary dust grains (Anders, 1989; see Figure 3). Grains released by comets at perihelion passage may be a major source of prebiotic molecules in the inner solar system (Brownlee and Kissel, 1990; Fomenkova *et al.*, 1994; Mumma *et al.*, 1996), although these may suffer some degradation in the interplanetary medium and significant heating on entering the Earth's atmosphere. Whereas organics enclosed within a meteorite may be afforded some protection, those within a small (1–100 μm), porous dust grain are generally much more vulnerable to vagaries of temperature and irradiation. Interplanetary particles currently reaching the Earth typically contain $\sim$10–20% carbonaceous material by mass, but their significance as carriers of prebiotics is not yet well-established (Gibson, 1992). They have been found to contain polycyclic aromatic hydrocarbons (Clemett *et al.*, 1993), a result which is probably of greater interest to astronomers than to prebiotic chemists! But, as in the chondrites, much of the carbonaceous material appears to be in the form of poorly characterized polymeric material (kerogen) or amorphous carbon rather than molecules of direct prebiotic relevance.

The delivery of organic matter to the Earth is discussed quantitatively by Anders (1989), Chyba *et al.* (1990) and Chyba and Sagan (1992). The current ($t = 0$) accretion rate of unablated carbonaceous matter is estimated by Anders (1989) to be $\dot{m}(0) \sim 3 \times 10^5$ kg/yr. If this rate is constant, then the timescale to accrete a mass equal to the current total biomass* is $\sim$2 Gyr. However, subject to caveats discussed in Section 3, it seems reasonable to suppose that the input flux of particles

* Timescale $\tau = m/\dot{m}(t)$, where $m \sim 6 \times 10^{14}$ kg is the estimated total mass of organic carbon in the biosphere (Chyba *et al.*, 1990).

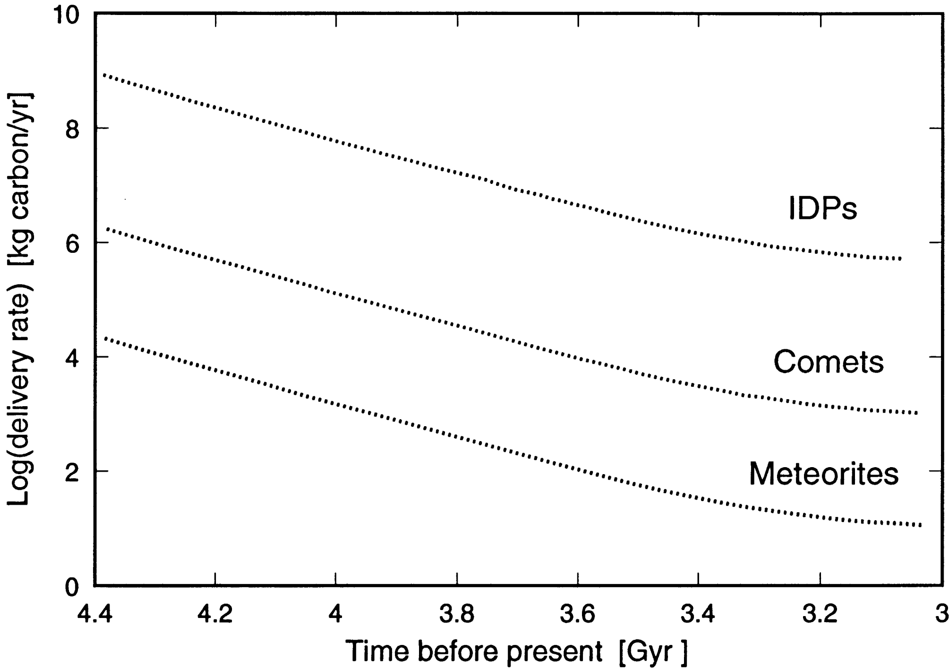

Figure 3. Exogenous delivery rates for organic carbon as a function of time, comparing interplanetary dust particles (IDPs), comets and meteorites. (Adapted from Chyba and Sagan, 1992).

was much higher during the period of late heavy bombardment compared with today. Assuming an accretion model based on lunar bombardment history (Chyba and Sagan, 1992), illustrated in Figure 3, the rate at epoch $t = 3.9$ Gyr was $\dot{m}(3.9) \sim 5 \times 10^7$ kg/yr, or a biomass in ~10 Myr. This approaches the endogenous production rate in the neutral (actually weakly reducing) atmosphere assumed by Chyba and Sagan.

Another consideration leads us to believe that the delivery rate might have been substantially higher in the distant past. If the early atmosphere was substantially denser than 1 bar, this would have broadened the size-range of particles sufficiently decelerated to preserve their organic content on passage through the atmosphere. A 10-bar CO_2 atmosphere has been proposed (Walker, 1985; Chyba *et al.*, 1990), and in this case the exogenous delivery rate may well have *exceeded* the endogenous production rate*. More importantly, a 10-bar atmosphere would have preserved the organic content of small comets (up to ~100 m in size); although not the dominant contributor to the total carbon influx (Figure 3), comets could have provided a particularly rich source of prebiotic molecules.

* Note that a denser atmosphere does not alleviate the problem of impact frustration, as the largest ($>$ 50 km) impacting bodies are not decelerated significantly from their cosmic speeds even in a 10-bar atmosphere.

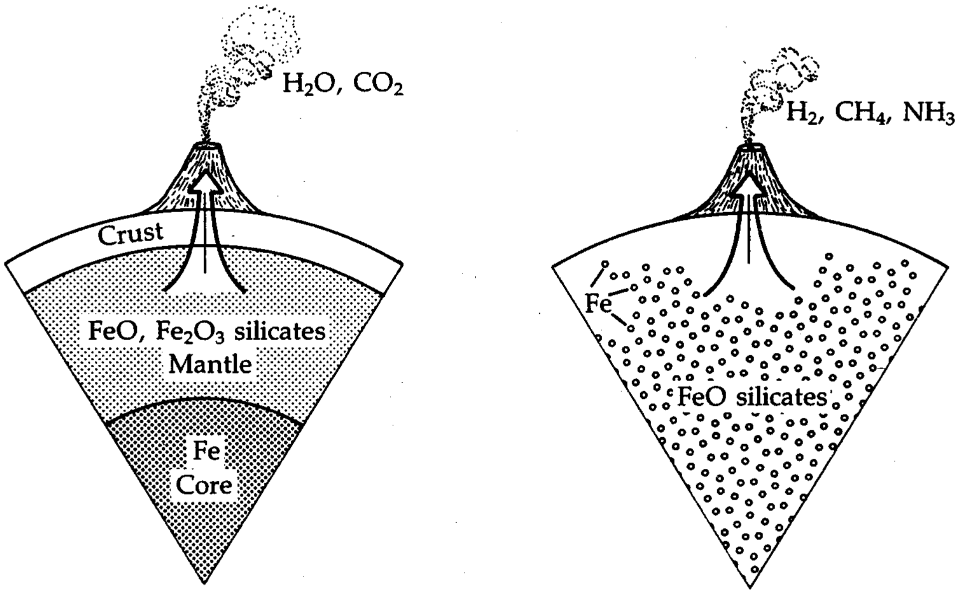

Figure 4. Contrasting views of the Earth's primitive atmosphere as related to internal structure. The loss of iron to the core (left) leaves the upper mantle in a highly oxidized state, leading to volcanic emissions composed primarily of H_2O and CO_2, as is the case today. If the Earth was originally more homogeneous in structure, with metallic iron present in the upper mantle (right), the emissions would tend to be more reducing and hence more conducive to prebiotic synthesis. (Adapted from Walker, 1986).

6. The Oxidation State of the Primitive Atmosphere

The composition and density of the Earth's early atmosphere is clearly a key issue. There is general agreement that the atmosphere originated by accumulation of gases released from the surface, and that its composition is closely coupled to that of volcanic emissions at any given epoch. These emissions are currently non-reducing (mostly CO_2 and H_2O), but might have been more reducing at an early epoch. If the mantle contained significant quantities of hydrogenated gases trapped from the solar nebula during the accretion process, then the earliest emissions could have been quite strongly reducing. However, gases of solar composition contain neon and nitrogen in approximately equal numbers; the extreme rarity of neon in the present atmosphere (and similarly other noble gases heavy enough to be retained) argues strongly against a major contribution from this source (Kasting, 1993, and references therein). Even so, H_2O provides a plentiful supply of hydrogen which might lead, through processes occurring in the mantle, to a mildly reducing early atmosphere. Free hydrogen, whether released directly or formed by UV dissociation of H_2O, NH_3 and CH_4, is subject to exospheric escape. Thus, unless continuously replenished, a reducing early atmosphere might not have been sufficiently long-lived.

The oxidation state of volcanic gases is likely to match that of the upper mantle where the gases originate (Walker, 1986; Kasting *et al.*, 1993). Figure 4 illustrates contrasting scenarios. The oxidation state of the mantle is characterized by the ratio of iron oxides to metallic iron. If the primitive Earth was relatively homogeneous in composition, with metallic iron present in the upper mantle, the early atmosphere may have been mildly reducing (right hand frame). Once the core formed, most of the Earth's endowment of iron became trapped in the core, leaving iron that remains in the mantle in a more highly oxidized state. The oxidation state of the upper mantle controls that of volcanic gases released from it (Kasting *et al.*, 1993). The present day mantle is highly oxidized, and present day volcanic emissions are composed primarily of water vapor and CO_2 with a dearth of CH_4 or free hydrogen. Whether the primitive atmosphere was reducing may thus depend on when the core formed. Did it form immediately, as part of the process that formed the Earth itself $\sim$4.6 Gyr ago, or did it accumulate at some later time by gradual separation of heavy and light materials? Current evidence strongly favors the hot accretion model in which the Earth essentially formed in a differentiated state (see Kasting *et al.*, 1993, and Gaffey, 1997, for reviews). If this is the case, non-reducing volcanic emissions are predicted from the earliest times.

Geological evidence provides some empirical support for the existence of a non-reducing atmosphere soon after the late bombardment. The Isua sediments (dated at about 3.75 Gyr), although highly metamorphosed, have been shown to contain carbonate deposits (Schopf, 1992), providing qualitative evidence for both surface water and atmospheric CO_2 at this epoch. In principal, a more quantitative investigation of the oxidation state of the early atmosphere is possible via geochemical analysis of igneous rocks (Kasting *et al.*, 1993). The abundance of chromium appears to be a particularly sensitive measure of original oxidation state (Delano, 1993); preliminary results suggest that ancient (3.5–3.8 Gyr) magmas have essentially the same high state of oxidation as those extruded in recent times.

7. Conclusions

Extraterrestrial matter delivered to the surface of the Earth may well have provided a significant, perhaps even dominant, source of prebiotic organic molecules available at the time of the origin of life some 3.7 Gyr or more ago. Two major uncertainties currently limit our ability to make a more definitive statement: (1) the Earth's impact history, and (2) the nature of the primitive atmosphere (its density and oxidation state) during the critical first 800 Myr.

The impact history and atmospheric density control the rate of delivery. Even with the most pessimistic scenarios, this rate was probably high enough to deliver a biomass of carbon and organics in a few hundred Myr. Much of this material may have been in the form of chemically inactive kerogens, but if the density of the atmosphere was as high as 10 bar or more, small comets rich in a variety of prebiotic molecules may have arrived non-destructively.

The efficiency of internal synthesis of prebiotic molecules is crucially dependent on the atmospheric oxidation state: production efficiencies fall dramatically for non-reducing (CO_2 and N_2 rich) atmospheres compared with those rich in hydrogenated gases such as CH_4 and NH_3. Geological evidence suggests (but does not yet prove) that the Earth's atmosphere was already non-reducing at the probable time of the origin of life. The exogenous delivery rate would probably have exceeded the endogenous production rate in a dense, non-reducing atmosphere.

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