Meteors as a Delivery Vehicle for Organic Matter to the Early Earth
(ESA SP-495)

P. Jenniskens

SETI Institute, NASA Ames Research Center, Mail Stop 239-4, Moffett Field, CA 94035-1000, USA

ABSTRACT

Only in recent years has a concerted effort been made to study the circumstances under which extraterrestrial organic matter is accreted on Earth by way of meteors. Meteors are the luminous phenomena associated with the (partial) ablation of meteoric matter and represent the dominant pathway from space to Earth, with the possible exception of rare giant impacts of asteroids and comets. Meteors dominated the supply of organics to the early Earth if organic matter survived this pathway efficiently. Moreover, meteors are a source of kinetic energy that can convert inert atmospheric gases such as CO₂, N₂, and H₂O into useful compounds, such as HCN and NO. Understanding these processes relies heavily on empirical evidence that is still very limited. Here I report on the observations in hand and discuss their relevance in the context of the origin of life.

1. INTRODUCTION

The origin of life on Earth is a difficult chemical problem involving organic chemistry of compounds more primitive than those dominating life today and in an environment that is quite alien to us. A key question has always been what chemistry predated the origin of life. Earth was formed in the hot inner parts of the solar system over a period of about 0.10 GYr at a time -4.55 GYr since the present. At the end of that period an impact with a Mars-sized protoplanet created the Moon. Earth was a hot, dry, and sterile place. In the next 0.1 GYr, the cratering rate was a factor of 10⁶ higher than today and decreased exponentially with a half life of 0.1 GYr. Between about -4.2 and -3.9 GYr (the accretion period called the "late veneer"), the cratering rate of large impactors gradually decreased so that water could condense into liquid water and organic matter could accumulate over periods of time. This impact rate leveled off around -3.6 GYr. Early signs of life date from as early as -3.8 GYr, suggesting that life formed as soon as conditions were favorable and that early life survived many giant impacts (see Thomas et al. 1997, and recent reviews by Mordibelli et al. 2000, Maurette et al. 2000, Robert et al. 2000).

The source of the water and organic matter on Earth can be traced through isotopes and dynamical models of planetesimal evolution. The water in our oceans has a D/H isotope ratio similar to that found in meteoritic matter. Because of that, it has been argued that most of Earth's water is from asteroidal origin. However, asteroid bombardment declined rapidly after the formation of Jupiter and was most significant when Earth was less than 60% of its final mass. Mordibelli et al. (2000) argued that the only sufficient source of water was a large planetary embryo originating in the outer asteroid belt that may have become part of Earth late in the accretion process (Wetherill 1992). I assume that this must have happened shortly before the Moon forming event at -4.50 GYr, which occurred when Earth already had >90% of its present mass. Much of the volatiles may have been lost in the collision and it is not clear how much and in what form organic matter would have been available at the surface. Since shortly after core formation, Earth had an oxidizing (water rich) mantle, I assume that much of the carbon would have oxidized and vented only as CO₂. Also, Mordibelli et al. point out that the neon content of Earth's atmosphere is a factor of 8-10 too high with respect to what would be expected in a scenario where all the rare gases and the water have been delivered by carbonaceous chondritic material.

More significant for the origin of life is what complex organic matter may have been available at the Earth's surface in the period of the late veneer. The long half-life of Moon impacts argues for comets being the dominant source for the late veneer. Delsemme (1997) and others have argued that comets in the Jupiter-Saturn region were the dominant source, based on dynamical time scales of planetesimal loss, but that is now disputed by Mordibelli et al. (2000). They rather suggest that comets in the Uranus-Neptune region and Kuiper Belt had the correct loss rate to account for the exponential decay of the Moon impact crater rate. The D/H ratio of these comets, however, is known from Oort-cloud comet observations and measured to be a factor of two higher than observed in Earth's oceans. The D/H ratio of the present day Earth argues for a cometary contribution not exceeding 12% of total and also the anticipated mass influx would have been less
than 10% of all available water (Mordibelli et al. 2000, Robert et al. 2000). D/H of the bulk of the organic matter tends to be slightly higher than for water in comets Halley and Hale-Bopp (Robert et al. 2000), so proton exchange with organics can not solve the D/H issue with oceanic water. The D/H of Jupiter-Saturn comets is not known, but is expected to be less because of more hydrogen exchange of the ice with the D/H poor protosolar nebula during grain accretion (Robert et al. 2000). It is possible, however, that much of the water predated these impacts, while the more significant complex organic matter was contributed by comets.

With the water, a lot of extraterrestrial organic matter was accumulated as well. Comets contain nearly as much mass in complex refractory organic matter (23 wt %) than water ice (31 wt %) (Greenberg 2000). Outer belt asteroids can contain up to 10 wt % of organic matter, and ~5 wt % water. The present day water content of Earth is ~1.4x10^24g (Delsemme 1992), while the amount of organic refractory matter in the total biomass is only about 6x10^17g (Chyba and Sagan 1997). Over time, most of the organic matter must have been oxidized into CO_2 and deposited in the form of carbonates. The carbon locked up in Earth's carbonate deposits is ~8x10^23g, and may be a relic of an early CO_2-rich atmosphere, up to 60 bars. It is not clear what was responsible for this oxidation. However, it is thought that the Earth had an oxidizing (water rich) mantle and most likely also an oxidizing (CO_2-rich) atmosphere very early on in its history. The production of reduced organic molecules in these conditions is difficult and that makes an exogenous source of the organic molecules more likely.

2. METEOROIDS AS A SOURCE OF ORGANICS

Of all exogenous sources of organic matter, dust particles can be the most important (Anders 1989, Chyba and Sagan 1992). Until recently, only "interplanetary dust particles" (IDPs) were considered, which represent grains small enough and slow enough to survive the accretion in Earth's atmosphere without melting or evaporating. IDPs are collected in Earth's atmosphere and can be studied in the laboratory (e.g. Rietmeijer and Nuth 2000).

Much more mass, however, is ablated in the Earth's atmosphere in a luminous phase called a "meteor". Figure 1 shows the present day influx rate of exogenous matter (Jenniskens et al. 2000, and references therein). The graph spans 35 orders of mass, from micron sized dust particles to tens of kilometers-sized asteroids and comets. The mass influx is dominated by three components: a) 100-200 micron sized meteoroids, b) asteroid fragments of ~ 4 meter (the magnitude of this peak is debated), and c) ~ 4 km sized asteroids and comets.

Figure 2 shows what happens to the infalling mass. Of all extraterrestrial matter small enough to not impact as a giant explosion, the bulk is deposited in the atmosphere rather than deposited as unmolten IDPs or meteorite fragments. Only 0.04 percent of asteroidal matter is found as meteorites and less than 8% of all particles smaller than 50 micron will end up as mostly unheated IDPs that can be collected in the stratosphere. Particles less than about 10 micron in size are evaporated as well, because they are thought to be so small that they do not efficiently radiate the heat from the air collisions.

Fig. 1. Yearly influx of extraterrestrial matter (from: Jenniskens et al. 2000)

Fig. 2 - The end product of impacts of various sizes (from: Jenniskens et al. 2000).
Meteoric ablation is the dominant fate of most infalling matter. Many of large 100-200 micron micrometeorites collected on the Greenland and Antarctic ice sheets (Maurette et al. 2000) show signs of melting and may well be a product of the meteor pathway. Solid debris, however, is only one form in which this matter is deposited in Earth’s environment. In particular, much of the volatile organic matter and water are lost from the meteoroids during this phase and will undergo their own characteristic chemistry before settling to Earth’s surface. Much of this paper is about those processes.

It is not clear if Figure 1 is representative for the mass influx at the time of the origin of life. The relative contribution of comets and asteroids may have been different, however. Surprisingly enough, there is much debate over the origin of the various dust components in the present day mass influx. About half of dust and half of large impactors appear to originate from the asteroid belt, but arguments are made that favor the dominance of either origin. The dynamics of comet dust loss is expected to be very similar now than it was at -4 GYr. The orbital dynamics may have been different however, which determines how much dust is lost before a typical impact occurs. More comets may have ended up in short-period orbits, loosing a larger amount of dust to Earth impacts, or less if dynamical conditions led predominantly to hyperbolic impacts. The cratering rate suggests that comet impacts dominated the Moon cratering and thus meteoroids may well have been correspondingly more abundant. The Moon impact record shows that the impact rate was a factor of 100 higher at -4 GYr and a factor of 500 higher in the 0.1 GYr following the formation of the Moon.

If the meteoroid influx was so much higher at the time of the origin of life, then meteoroids represent sufficient organic carbon to account for all carbon in Earth’s carbonate deposits and sufficient solar wind implanted Neon to account for the Neon in Earth’s atmosphere, but possibly too little water to account for Earth’s oceans (Maurette et al. 2000). In light of the efficient loss of organics from the Earth environment, meteoroids are important by providing a continuous source of complex organic molecules to such environments as the ocean surface.

3 THE DEPOSITION OF ORGANIC MATTER BY METEORS

The organic carbon has its origins in accretion processes in the interstellar medium (Jenniskens et al., 1993), while a small fraction originates in the atmospheres of late-type stars. The GIOTTO and VEGA spacecraft probes measured the elemental composition of dust grains in the coma of comet Halley and found many to be rich in the elements C, H, O and N (Kissel and Krueger, 1987; Jessberger and Kissel, 1991). This organic carbon was mixed intimately with the silicate component and has high molecular mass. Most of it is expected to survive exposure to the vacuum of space and will only be gently warmed when grains come as close to the Sun as Earth’s orbit ($T_{\text{max}} \approx 300$ K). Organic matter in Interplanetary Dust Particles is typically lost only after heating to 600-800 K.

| TABLE I |

<table>
<thead>
<tr>
<th>source</th>
<th>amount (kg/yr)</th>
<th>ref.</th>
</tr>
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<tbody>
<tr>
<td>Exogenous:</td>
<td></td>
<td></td>
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<tr>
<td>IDP</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Meteors (if 100 % C survives)</td>
<td>$2 \times 10^6$</td>
<td>[1]</td>
</tr>
<tr>
<td>(Micrometeorites)</td>
<td>$1 \times 10^9$</td>
<td>[2]</td>
</tr>
<tr>
<td>Meteorites*</td>
<td>$2 \times 10^8$</td>
<td>[3]</td>
</tr>
<tr>
<td>Comets/Asteroid impacts</td>
<td>$1 \times 10^6$</td>
<td>[1]</td>
</tr>
<tr>
<td>Atmospheric:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Meteors (if LTE, V-[OI])</td>
<td>$&lt; 1 \times 10^9$</td>
<td>[2]</td>
</tr>
<tr>
<td>Comet/asteroid impacts</td>
<td>$2 \times 10^6$</td>
<td>[1]</td>
</tr>
<tr>
<td>Electric discharge</td>
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<tr>
<td>(mild reducing atmosphere)</td>
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<td></td>
</tr>
<tr>
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<tr>
<td>Hot or cold springs</td>
<td>(CH4 only)</td>
<td>[4]</td>
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Whether the meteor pathway is important for the delivery of organic matter to the early Earth depends on how efficiently the organic matter survives the ablation process in some usefull form. In Table I, my own estimates for the delivery of organic matter from meteors (Jenniskens et al. 2000) are compared to estimates from Chyba and Sagan (1997), Mojzsis et al. (1999) and Maurette et al. (2000), without an effort to re-evaluate the latter. Until now, meteors were not considered in such evaluations, because it was generally assumed that the material that is ablated is destroyed (read: converted to CO$_2$). However, if organic matter survives ablation efficiently (Table I), meteors may have contributed more than 2/3 of all infalling organic matter.

Meteors are also potentially efficient sources of energy for atmospheric chemistry, with estimated production rates in Table I if the plasma is in chemical equilibrium and the volume is represented by the measured OI line intensity (Jenniskens et al. 2000, see below).
3. Ablation at high altitude

Classic models of meteor physics assume that the meteoroid is gradually heated by collisions with air molecules until the particle melts and starts to evaporate individual compounds in order of sublimation temperature. This model is called differential ablation. Because it takes some time for the more volatile compounds to diffuse outwards, each compound is lost over a range of altitude. Figure 3 shows calculations by Elford et al. (1997). The volatile organic material would be lost predominantly at about 117 km in the case of Leonid meteors. More volatile components would come out even higher.

Unusual ablation at a record height was discovered by Spurny et al. (2000), who reported the discovery of high altitude emissions in bright Leonid fireballs. Above 136 km, the meteor looks like a V and must emit very efficiently to explain the observed luminosity. This high-altitude luminosity is probably associated with plasma interaction of electrons emitted in the collisions with air molecules. Only compounds near the surface can be lost as a result of the violent collisions of air molecules with the meteoroid.

Evidence for the differential loss of organic matter was reported by Rossano et al. (2000), who detected a bright infrared flare in the mid-IR images of two meteors. Those flares occurred at 115 and 117 km altitude, respectively, which would be consistent with the release of organic material. The mid-IR intensity was ten times the brightness of the meteor in the optical. However, no spectrum has been recorded yet and it is not certain that this unusual emission was due to the organic matter in the meteoroid.

3.2 Ablation at moderate altitudes

Borovicka et al. (1999) did report the early release of a sodium-containing mineral in Leonid meteoroids that were ejected only 100 years ago, consistent with differential ablation. Similar behavior is now known from Draconid and Ursid meteoroids, all from relatively recent ejecta. This phenomenon was linked to the fragile nature of the Leonids meteors that may expose the volatile minerals more efficiently. In fact, most meteors show a simultaneous release of all mineral components, suggesting that also the organic matter is mostly deposited at moderate elevations of 70-110 km altitude, and mostly around 85-90 km where ~150 micron meteoroids with typical 25 km/s entry velocities tend to ablate. There, the organics are shielded from the most ionizing UV radiation and will ultimately settle to the ground.

Three stages need to be considered for the survival of organic matter during deposition at these moderate altitudes. First of all, the impact of air molecules can potentially strongly heat the molecules near the head of the meteor and destroy the compounds. Secondly, the molecules reside for a short period of time in a hot...
meteor plasma. A plasma temperature of 4,300 K was measured from the N$_2$/N ratio in high resolution Leonid spectra during the 1998 Leonid MAC mission (Jenniskens et al. 2000). That temperature was similar to the $\sim$4500 K temperature measured for the metal atom ablation lines of Fe and Mg (Abe et al. 2000).

Third, once the molecules have cooled they are affected by the ambient chemistry in the upper atmosphere, before sooner or later coming down to the surface.

We used Direct Simulation Monte Carlo techniques to study the rarefied flow field about a meteoroid and the physical conditions in an effort to understand the relatively moderate temperature of 4300 K (Jenniskens et al. 2000, Boyd 2000). We also studied the conditions near the head of the meteoroid, where densities are high, using classical hydrodynamic codes to understand the ablation process (Popova et al. 2000).

What happens when a complex organic molecule is sputtered off the surface of a meteoroid? Initially, chances are that it will be close to the meteoroid surface where it can undergo a number of collisions at a relatively low temperature, less than the evaporation temperature, about 1,400 K. More than half of the matter are reducing compounds from the meteoroid. When organic carbon, containing some fraction of nitrogen and oxygen, is heated to high temperatures, or sputtered by fast ions or energetic photons, small fragments are lost such as H, O, H$_2$, O$_2$, OH, H$_2$O, CO, CO$_2$ and CH$_4$ in a process called carbonization (Jenniskens et al., 1993; Fristrom, 1995, p. 318). Further heating (up to 700 K) leads to further loss of H and H$_2$ in a process of polymerization, with growth of aromatic ring structures, and some graphitization by stacking of those rings (e.g. Koidl et al., 1990). Ultimately, temperature increase leads to decomposition by loss of H$_2$, CN, CH, C$_2$, and C$_2$H. Hydrocarbon radicals higher than C$_2$ are so excited by
their formation that they rapidly fission into lower products, leaving only the thermally stable single and double carbon radicals, unless prevented by rapid radiative cooling. Carbon atoms are present too, but at lower abundance because of thermodynamic considerations (Rairden et al. 2000).

It is not clear, how much decomposition of organic molecules will occur in the head of the meteor. After being accelerated by even a single collision, the molecule will stream along the wake line, mix with heated air molecules and expand in volume, during which the average temperature will gradually increase to the plasma temperature of 4,300 K (Figure 6). The temperature increase is more rapid at lower altitudes. The meteoric material represents about 1% of the material in that meteor wake. At the collision frequencies occurring in the wake (~25,000-50,000 sec⁻¹) a compound will generally undergo 25-50 collisions before quickly (time scales of ~1 msec) cooling down to modest temperatures (Boyd 2000). Each collision (which has to be with the right species in the right orientation) will generally remove only one atom from an organic compound under the type of radical chemistry that will be occurring. This can be particularly important for larger organic compounds such a PAHs (polycyclic aromatic hydrocarbons) that will need more than a few collisions to be destroyed.

The products of this chemistry are different from the original organic compounds in the meteoroid. Notably, they will contain more entrained oxygen, potentially leading to usefull compounds for prebiotic chemistry. However, their chemical evolution has not stopped. Once the plasma has cooled, the meteoric matter will reside in the upper atmosphere for long periods of time. These compounds can then become mixed with the atmosphere, engaging in photochemistry, before finally settling to the ground.

In an effort to understand the fate of organic matter in this process, one could search for mid-IR emissions from complex organic matter in the meteoroid or for the molecular breakup products that cause emissions at optical wavelengths. Of all breakup products, the CN radical is the most easily detected because of a strong B → X transition of low energy potential. This electronic transition has a band head at 388.3 nm in the near ultraviolet, but also many nearby iron atom emissions. An upper limit of [CN]/[Fe] < 0.32 at 4,300 K was derived from the best observations -2 magnitude Leonid meteor observations to date (Rairden et al. 2000), which translates to less than 1 CN molecule is present per three Fe atoms in the meteor plasma. Comet Halley's dust has a nitrogen abundance of [N]/[Fe] = 0.79 ± 0.02 (Delsemme, 1991). All of that nitrogen is part of the organic carbon. Our upper limit suggests that half of the nitrogen survives the ablation process. However, nitrogen and iron may also be released in other form than studied here. Clearly, this upper limit has to be improved upon. No infrared spectrum of a meteor has been obtained so far.

3.3 Deposition as debris

Organic debris is found in many large micrometeorites that are collected at the Earth's surface (Maurette et al. 2000). If the particle is not completely melted, or the organic matter has not sufficient time to diffuse out of the melt, then some of it can survive the accretion process as a solid particle.

Until recently, this process was not observed in-situ at altitude. Now, Borovicka and Jenniskens (2000) reported that a 1-kg Leonid fireball, with sufficient kinetic energy to break every single bond in the meteoroid a thousand times, was found to leave debris in its path. An afterglow emission was observed that consisted of metal atom emissions but not the usual atomic lines of oxygen and nitrogen of the air plasma. A continuum emission was observed as well, with a blackbody temperature of 1,400 K, the melting temperature of chondritic material.

From persistent emissions in the path of the same fireball at 84-km altitude several minutes later, Russell et al. (2000) reported a continuum emission and the possible detection of a C-H stretch vibration band. This important result awaits further study, but would be consistent with the intimately mixed organic matter surviving the breakup process.

4. AEROTHERMOCHEMISTRY

Meteors are also a potential source of energy for interesting aerothermochemistry in an N₂/CO₂ rich early-Earth atmosphere (Table I). The violent collisions and high plasma temperatures break molecular bonds and rapid cooling can result in a significant yield of small molecules such as NO, CN and C₂. In fact, Local Thermodynamic Equilibrium (LTE) abundances of such compounds peak at the observed plasma temperature of 4,300 K (Figure 7). We discovered that the meteor wake temperature is just high enough to break CO₂ into its atomic constituents, without ionizing the atoms (Jenniskens et al. 2000).

To estimate the yield of this process is not easy. Non-equilibrium conditions may affect the outcome of the process. The meteoritic material entrained is fairly reducing and can lower the net redox level of the meteor's train, which alters the chemistry during cooling. Also, many processes affect the total volume of air that is affected.
The plasma volume has to be derived from measurements. Jenniskens et al. (2000) measured from the intensity of OI line emission an effective volume 10^6 times larger than expected for a spherical cloud with the classical initial-radius. Part of that is understood from the formation of a warm wake behind the meteor, part may also be simply a result of non-LTE conditions in the air plasma. To complicate matters, the meteoroids were found to eject small bits and pieces to distances up to 2 km away from the cm-sized meteoroid (Taylor et al. 2000).

The non-detection of the 389 nm CN emission band sets an upper limit to the volume of the air plasma for -2 magnitude Leonid meteors. The calculated CN abundance for a 4,300 K air plasma in LTE at 95 km altitude for a total concentration of CN equals 1.0x10^5 molecules of CN per cubic centimeter for a -2 magnitude Leonid, or an expected [CN]/[Fe] of about 5 x 10^-5. However, if the plasma volume is as large as inferred from the OI emission intensity, this would increase the [CN]/[Fe] to 50 atoms / cm^3, a factor of 150 above our detection limit. If LTE applies, the observations suggest that the expected yield for atmospheric processing to CN by meteors in Table I is only 7 x 10^5 g/yr, much less than other estimates. However, we assumed an oxidizing CO_2 rich atmosphere and little nitrogen and the yield of NO would be significantly higher in a mildly reducing atmosphere or an atmosphere more rich in nitrogen as assumed to estimate the yield of other mechanisms.

Moreover, the chemistry in the wake is significantly affected by the entrained meteoric matter. This material is generally made up of reducing species (metallic/ferrous iron, reduced organics, sulfur/sulfides, etc.) and it will lower the redox level of the meteor's train, reducing the number of oxidizing reactants. For most of these species, the stoichiometry of oxidation is greater than 1:1 and each molecule of meteoritic material can consume more than one oxygen atom. Organic molecules can consume dozens or more. This has the potential to shift the products of such processing away from the usual NO and CO that one typically sees from a non-reducing atmosphere to those one might see for a more reduced atmosphere. Probably the two most important sources of oxygen during such heating are carbon dioxide (which gives up an oxygen to form carbon monoxide) and molecular oxygen itself. In an early Earth's atmosphere, there should be enough meteoritic material entrained to compensate for an atmosphere containing up to several percent of such species depending on stoichiometry and composition of the meteoroid.

5. ORGANIC MATTER IN INTERPLANETARY MEDIUM.

No discussion of the fate of organics is complete without considering the chemical evolution from organic matter in comets to organic matter in the meteoroids just before accretion. Of interest are chemical changes that may occur by exposure to sunlight and solar wind during the period from comet ejection to Earth impact. Of interest is our recent find that freshly ejected meteoroids tend to break apart more easily than meteoroids that spend thousands of years in the interplanetary medium (Murray et al. 1999, Borovicka et al. 1999). This suggests that freshly ejected grains (which just have lost the ice between the grains) are fluffier and face a gradual compaction with subsequent heating/cooling cycles and solar wind exposure. However, no such things seem to happen. Based on the observed effect of radiation pressure on the location of the dust grains in the comet dust trail, I derived a density of 0.97±0.13 g/cm^3 for Leonid meteors (Jenniskens 2001), in good agreement with the density of about 0.7 g/cm^3 derived by Spurny et all (2000a) from the deceleration of a meteor in the Earth's atmosphere. Surprisingly enough, these densities are similar to those the older Perseid and Taurid
meteoroids. It appears that exposure to the interplanetary medium does not affect the surface-to-mass ratio of the particles as much as the adhesiveness of the rocky subunits in the meteoroid. It is possible that the organic matter becomes more sticky over time, sintering occurs, or the grains subtly increase their VanderWaals contact areas.

Clearly, much has been learned in recent years about the evolution from organic matter in small solar system bodies to organic compounds in the early Earth environment, but much is still to be learned. Future Leonid MAC missions and ground-based observations may shed further light on this matter.

This work was supported by a grant from NASA's Exobiology Program.

9. REFERENCES


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