Evolution of Interstellar Dust and its Relevance to Life’s Origin: Laboratory and Space Experiments

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Abstract A scheme is presented for an analog investigation of long term irradiation of ices and organics following the cyclic evolution of interstellar dust. The irradiation is proposed to be performed at cryogenic temperatures on a space platform, and with an enhancement of the solar ultraviolet flux using a concave mirror, grating combination which eliminates the visual and infrared from the sample surface.

1 Introduction
A major change in our ideas about life’s origins has taken place in the past 25 years. Whereas it was once thought that the major prebiotic chemistry was based exclusively on processes occurring in the earth’s atmosphere (Miller, 1953) it is now generally accepted that the major sources of prebiotic molecules originated in the distant space between the stars. The early earth’s atmosphere was almost totally oxidizing rather than reducing and was therefore unsuitable for the abundant formation of even such molecules as formaldehyde. On the other hand we have astronomical evidence that this can be a relatively significant molecule in the interstellar dust as well as in the gas (Schutte, 1998; van Dishoeck, 1998). In addition, as had been predicted by Greenberg et al. (1972) there is now abundant evidence for the presence of huge quantities of complex organic molecules in the interstellar dust observed as an infrared absorption feature at 3.4 μm characteristic of CH stretches in CH₂ and CH₃ groups in aliphatic hydrocarbons. These, of themselves, are not necessarily prebiotic but, as indicated by the results of laboratory experiments, mimicking the processes in interstellar space, they are only the “tip of the iceberg” in accounting for a major organic constituent of the interstellar dust (Greenberg 1998a). With the advent of the proof of the presence of chiral organic components in a meteorite which are clearly extraterrestrial in origin and which have left favoring enantiomeric excesses as high as L/D = 2 (Cronin and Pizzarello, 1997; Engel, Macko, and Silfer, 1990; Engel and Macko, 1997) we have even further evidence for an extraterrestrial source of prebiotic molecules which are not only chemically suitable but which also bear the “correct” left handed signature of handedness of the amino acids of all living creatures.

While it has been correctly argued that comets are not the greatest contributors of organics to the earth’s surface (Chyba & Sagan 1992) we believe it is incorrect to use this fact to imply that comets are not the most likely contributor to the origins of life. We use the plural of the word origins because it is more likely than not that the way comets delivered prebiotic organics to the earth, and undoubtedly also to Mars, the beginning of life had a multitude of chances both in time and space. The problem of demonstrating this devolves itself into showing how the chemical composition, the chirality and the morphology of comet organics and comet dust combine to provide appropriate packages of complex organics which when landing in water provide highly concentrated, albeit small, volumes of prebiotic chemical evolution sites.

The story starts with the chemical evolution of tenth micron interstellar dust grains in the clouds of gas and dust in space, how they become chiral, how they coagulate in the protosolar nebula into comets and how the fragile fluffy nature of comet nuclei provides the physical basis for “gentle” delivery of comet organics to the earth.

In this paper we will emphasize the laboratory and space analog experiments which may be used to prepare prebiotic molecules which closely resemble those made in interstellar dust and whose analysis will prepare us for the study of cometary materials either in situ as planned for the Rosetta mission or “in house” as planned for some NASA missions. Finally, we propose a new way to use the international space station to provide the best means for preparing organic material analogues similar to those which may have been the precursors of life in the universe.
A cyclic evolutionary model of interstellar dust

Interstellar dust is certainly not static as is implied by some modeling of the interstellar extinction. Each dust grain, during its lifetime, passes through a wide variety of environments and interactions both constructive and destructive. The initial phase occurs in the atmospheres of cool evolved oxygen rich stars. Here small silicate particles are produced and ejected into the surrounding interstellar space. Once these silicate particles escape they immediately cool down to temperatures of 10 – 15 K and become coupled to the gas as part of the general interstellar medium. Ultimately, the gas cloud containing the silicate particles becomes denser and the rate at which atoms and molecules collide with the grain is sufficient to grow a mantle. Simple molecules like H$_2$O, CH$_4$, NH$_3$ form initially by surface reactions of the colliding O, C and N with H. Additional molecules - predominantly CO - accrete as such, although surface reactions with hydrogen may also lead to HCO and H$_2$CO as well as CH$_3$OH.

Over the $3 \times 10^7$ years in a molecular cloud the ultraviolet photo-processing produces a complex organic component in the mantle as the molecules are broken and recombine. While the cloud is dispersed - usually as a result of star formation - and subsequently, when the dust grain is in the diffuse cloud phase, it loses its volatile mantle components leaving only the complex organic refractory component. This “first generation” organic material is then subjected not only to the 10,000 times as intense (as in the molecular cloud) radiation field it is also subjected to the destructive processes accompanying supernova shocks (Draine & Salpeter 1979; McKee 1989). The resulting and remaining organic material is what is observed in diffuse cloud dust. The destruction by shocks and grain-grain collisions probably result in breaking off pieces of the organics which are then to be observed as very small carbonaceous particles and large molecules (PAH’s) contributing to the ultraviolet and far ultraviolet extinction. This completes one cycle.

Unless the grain is consumed by star formation or has become a part of a planetary/cometary object in a “solar system” it may pass through a series of diffuse cloud/molecular cloud cycles, only the first one starting with “pure stardust”. The ultimate fate of a dust grain will be via star formation. The maximum mean lifetime of a grain is then the mean turnover time for the interstellar medium which is about $5 \times 10^9$ years so that each grain, on the average, should have undergone about 50 complete cycles.

In Fig. 1 is shown schematically how the various organic components of the interstellar dust evolve, starting with the diffuse cloud interstellar dust. In addition to the tenth micron silicate core-organic refractory mantle particles there are thousands of small carbonaceous particles responsible for the 220 nm extinction hump and many more even smaller particles presumed to resemble PAH’s which are responsible for the far ultraviolet extinction (Li & Greenberg 1997). As the density of the cloud increases in the transition to the molecular cloud phase, an icy mantle grows and traps some of the hump and PAH particles. The accompanying ultraviolet effects on the ices leads to interactions with the inner organic mantle which modifies it, as indicated by the missing 3.4 μm feature. It also provides a source of interactions between the radicals produced in the ices and the hump and PAH particles changing their character as well. At the same time, the ultraviolet is producing the beginnings of first generation organics in the ices. The transition back to the diffuse cloud phase occurs with a very substantial increase in the ultraviolet photoprocessing. In fact, it could well be that the major processing of the ices leading to first generation organics occurs in the transition phase; i.e., before the ices evaporate or are sputtered away they are subjected to ultraviolet fluxes 1000 – 10,000 times greater than in the molecular cloud. Finally, while the ices are being destroyed in the diffuse cloud, the precursors of the ultimate hump particles and the ultimate PAH’s emerge. These are

![Fig. 1 Schematic of evolution of the organic component of interstellar dust. DC = diffuse cloud phase; MC = molecular cloud phase; OR = average diffuse cloud organic refractory mantle material; OR$_1$ = “first generation” organics; components with a superscript (’) are modified forms. See text for additional descriptions.](image-url)
now intensively processed by the ultraviolet and resume their diffuse cloud character as “normal” hump and far ultraviolet (PAH) particles. The same intensive ultraviolet modifies the outer first generation organic mantle as well as the inner organic mantle, resulting in the highly processed organic refractory diffuse cloud dust mantle.

The cometary material is schematically indicated as resulting from aggregates of the molecular cloud dust and, as such contains both processed and first generation organics as well as the ices, hump and PAH particles, the latter being trapped in the ices.

3 Laboratory analog organics

The use of laboratory methods to produce and study possible organic or carbonaceous constraints of interstellar dust has become very important. Here we limit ourselves to: (1) the residues produced from ultraviolet photoprocessing of ice mantles as an analog to the material made in the molecular cloud phase (“first generation” organics) and (2) the (solar) ultraviolet irradiated residues as an analog to the diffuse cloud carbonaceous mantles (higher generation organics).

The chemical and physical analogues of first generation organics (molecular cloud phase) suggest that such material is relatively rich in oxygen. They are rich in molecules of a clearly prebiotic nature, including the amino acids glycine, serine and alanine, as was shown in a GCMS analysis (Briggs et al. 1992; also see Kobayashi et al. 1995). The first generation organics do not provide a perfect match to the interstellar 3.4 μm feature (see Greenberg et al. 1995 and references therein). In order to approach the true diffuse cloud organic mantle material some of the laboratory residues were subjected to 6 months exposure by solar ultraviolet irradiation on a space platform. These materials provided excellent 3.4 μm spectra (Greenberg et al. 1995). While the mass spectral analysis of the material is still preliminary the indications are that it is rich in polycyclic aromatic hydrocarbons.

4 Cometary organics

The first direct observational confirmation of the prediction (Greenberg 1979, 1982) of complex organics in comets came from the mass spectral data obtained for comet Halley dust (Kissel et al. 1986a, b). Further analysis of the data showed that the organic molecules had, on the average, a higher initial energy than the silicate ions which led Krueger & Kissel (1987) to infer a core-mantle structure of the dust particles. Thus according to Jessberger & Kissel (1991) “The existence of the previously postulated (Greenberg 1982) core-mantle grains seems to be substantiated by data”. An O : C = 0.6 : 1 ratio deduced from the overall comet Halley organics is much higher than deduced from the Galactic center absorption spectra but is consistent with a mixture of first generation laboratory organics with space irradiated organics as implied by the lab residues returned after being exposed to the sun for 6 months (Greenberg et al. 1995).

If we assume that the comet material contains the solar system abundance of the elements and if we assume that the Si, Mg and Fe are totally bound up in the silicate cores we may derive a mantle to core mass ratio. This turns out to be (Greenberg 1998b) \( m_{\text{mantle}}/m_{\text{core}} = 1 \) which is in agreement with the value obtained by the Giotto/Vega space mission to comet Halley (Krueger & Kissel 1987) as well as with the BN polarization requirement if \( \rho_{\text{an}} \approx 1/2 \rho_{\text{el}} \) (Greenberg & Li 1996a).

5 Comet dust as seeds for life’s origins

Krueger & Kissel (1989) have suggested how small comet dust grains (3-5 μm in size) made up of highly porous aggregates of silicate-core organic refractory mantle particles as pictured by Greenberg & Hage (1990) and schematically shown in Fig. 1 of Greenberg (1998b) as diffuse cloud dust fulfill the requirements for chemical thermodynamics to start molecular organization. Each comet dust particle sitting within a water bath (the primitive ocean) satisfied the conditions for non-equilibrium thermodynamics as in Nicolis & Prigogine (1977). Now, as we picture the additional advantage of homochirality, there appears to be an even greater probability that each comet dust grain provided a seed for life’s origins. Furthermore, even if each comet of 3 km radius deposited only 0.1% of its mass as comet dust in the appropriate size range there would have been 10^25 such seeds (Greenberg & Li 1996b). One comet Halley could have provided 10% of the current biomass of the earth in the form of complex organics.

6 Space irradiation at cryogenic temperature

The results of the first space irradiation experiments on organics already proved to be very useful in understanding the chemical evolution processes occurring in interstellar dust, even though restricted in time and temperature. To fully understand the creation of prebiotic materials in interstellar space we have to go to the next step of not only creating the right temperature condition but also the full equivalent time conditions.

The photoprocessing of interstellar dust mantles occurs in basically two environments: diffuse clouds, molecular clouds. In both cases the grain temperature is low, being as low as 5 K in the cores of molecular clouds and nominally about 15 – 20 K in diffuse clouds (Greenberg & Li 1996c). However, not only are the environmental conditions different but also the grain mantles themselves. In molecular clouds the mantles consist of a variety of frozen molecules, commonly called ices, where H2O and CO are generally the most abundant constituents. In diffuse clouds, the ices are not present and the mantles are best characterized as consisting of complex organic material dominated by carbon but containing various amounts of O, H and N depending on the grain history (see Greenberg 1998a, Schutte et al. 1998).

The interstellar physical conditions are simulated in the laboratory by the combination of a cryostat, a vacuum
ultraviolet lamp and a gas source. Simple gases are deposited on a cold finger in the cryostat and irradiated by ultraviolet. The first approach to this problem was taken some 30 years ago with the result that complex organic molecules were shown to be readily created from the effects of ultraviolet radiation on simple ices if followed by warming up (Greenberg et al. 1972). The first laboratory dedicated to creating and studying the interstellar mantles which result from ultraviolet photoprocessing was the Leiden Astrophysics Laboratory. For details of the system see Hagen et al. (1979). The major advantage of the laboratory analog is provided by the ratio of the lamp UV flux ($\Phi_{is}^{UV}$) to that in the interstellar medium ($\Phi_{is}^{UV}$)

$$\Phi_{is}^{UV} \equiv 10^{15} \text{cm}^{-2} \text{s}^{-1}$$

$$\Phi_{is}^{UV} \equiv 10^{3} \text{cm}^{-2} \text{s}^{-1}$$

where UV means for all ultraviolet wavelengths such that $\lambda \leq 200 \text{nm}$ ($E \geq 6 \text{ eV}$). Thus one hour in the laboratory is equivalent to about 1,000 years in the diffuse cloud and about $5 \times 10^5$ years in a molecular cloud. Unless one provides higher vacuum conditions than normally available in the laboratory ($\sim 10^{-5} \text{torr}$) we are limited to irradiation times $\sim 24$ hours before significant contamination occurs. This is adequate for the full time simulation of a mean molecular cloud phase duration ($\sim 3 \times 10^7$ yrs) but is totally inadequate to simulate the diffuse cloud phase which is also $\sim 3 \times 10^7$ yrs but with fluxes 10,000 times higher.

The major advantages of using the solar ultraviolet in space to simulate the diffuse cloud dust mantle evolution are: (1) many samples may be irradiated simultaneously, (2) longer effective irradiation times are feasible. This was well demonstrated by the results obtained on the ERA (Exobiology Radiation Assembly) platform of the EURECA satellite for the irradiation of laboratory residues simulating the organic mantles created in the molecular cloud. Note that the solar flux at $\lambda < 200 \text{ nm}$ is only $\Phi_{s}^{UV} \equiv 2 \times 10^{14} \text{cm}^{-2} \text{s}^{-1}$ so that equivalent exposure times are 50 times longer than in the laboratory. However, even though the 6 months space exposure (total 4 months exposed to solar UV) was equivalent to only about $10^7$ years in the ISM it already showed how important its effect was because for the first time we were able to obtain a laboratory created material which really gave the observed interstellar 3.4 $\mu$m feature (Greenberg et al. 1995). However, the experiment was not completely correct because it was done at ambient temperatures rather than cryogenically. Cryogenics is clearly difficult to achieve under direct solar radiation, so how can we achieve it on a space platform? The answer is: first put the sample to be irradiated in the shadow then use reflected sunlight from which all but the ultraviolet has been reflected away from the sample. This is done with a grating. However, as long as we are using a mirror, why not use a condensing mirror and amplify the solar flux? The essentials of the proposed method are discussed in the following sections.

6.1 Laboratory analog requirements

a) Temperature

The mean temperature of dust grains in molecular clouds is $T_{mc} = 5 \pm 10$ K and in diffuse clouds is $T_{dc} = 15 \pm 20$ K (Greenberg & Li, 1996c). The mean temperature of Titan aerosols is $T_1 = 100$ K. These temperatures are easily achieved in the laboratory.

b) Time

In the interstellar medium, the dust shuttles between its diffuse and molecular cloud phase with time spent in each of $\sim 3 \times 10^3$ yrs. The total UV fluence experienced in the diffuse and molecular cloud phases respectively is

$$F_{dc} = 10^{23} \text{h} \text{v} \text{ cm}^{-2}$$

$$F_{mc} = 10^{19} \text{h} \text{v} \text{ cm}^{-2}$$

The laboratory analog photoprocessing times ($\tau_{op}$) required to achieve $F = 10^{23} \text{cm}^{-2}$ and $F = 10^{19} \text{cm}^{-2}$ are $\tau_{op}^{dc} = 3$ yrs. $\tau_{op}^{mc} = 2.6$ days, respectively. The former is clearly out of the acceptable laboratory range while the latter is just about the laboratory limit.

6.2 Space analog requirements

a) Amplification and UV selection

A highly schematic diagram showing the essentials of the idea of using the shadow and a converging mirror is shown in Fig. 2. A much more detailed version has been developed by Hashimoto (1998). For the essentials of this discussion Fig. 2 should suffice. The mirror should be placed such as to provide a broad beam equal in area to the sample. This leads to an amplification factor of

$$A = \left( \frac{D_{mt}}{d_s} \right)^2$$

where $D_{mt}$, $d_s$ are the diameters of the mirror and the sample covered region, respectively. The mirror surface is a reflection grating such that only the ultraviolet with $\lambda < \lambda_1$ (where $\lambda_1 = 200 \text{ nm}$) reaches the sample. Note that it would be desirable to use another plane mirror whose diffraction reverses the spectrum so that the average ultraviolet illumination is spread across the sample. Such details are considered in the Hashimoto (1998) design.

b) Heating reduction

The total solar flux is reduced according to

$$R = A \left( \frac{\Phi_{is}^{UV}}{\Phi_{total}^{UV}} \right)$$

where, at the earth $\Phi_{is}^{UV}(<200 \text{ nm}) = 0.17 \text{W m}^{-2}$, and $\Phi_{is}^{UV} = 1.36 \times 10^4 \text{W m}^{-2}$. Thus, for an amplification factor $A = 100$, $R = 1.25 \times 10^2$ so that cryogenic cooling is 100 times easier. If we wish to allow longer wavelengths to be used, say $\lambda < 256 \text{ nm}$, the reduction factor is still 0.1.
c) Amplification limitation

The degree of amplification is limited not only by the heating but also by the necessity to avoid two photon processes. The rate of photon absorption should be such that the time between photon collisions is longer than the relaxation time of excited molecules to decay to the ground state. An upper limit on this relaxation time is the infrared emission time $t_{\text{rel}} < 10^{-3}$ s. The time for double solar UV photon processes is

$$t_{\text{sun}} \geq 10^{21} \text{s}$$

assuming the molecular absorption cross section for UV is $\sigma_{\text{UV}} \leq 2 \times 10^{-16} \text{cm}^2$. This is many orders of magnitudes larger than the relaxation time. Thus the allowed amplification is $A \leq 50/10^{-3} = 5 \times 10^4$ which would in any case probably be too high for cryogenics. However, in the case of simulating Titan aerosols, the temperature requirement is far less restrictive than for the interstellar analog.

7 Concluding remarks

Effective solar ultraviolet irradiation equivalent to times of $3 \times 10^7$ years in the interstellar medium at cryogenic temperatures of 10 K is achievable with the proposed system on time scales of a month as compared with the required 9 years under the condition of the EURECA ERA platform. The equivalent of the ERA irradiation of 6 months could be achieved in 2 days so that the EURECA type irradiation experiments could easily be performed on a shuttle.

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