

# On the formation and survival of complex prebiotic molecules in interstellar grain aggregates

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**Abstract:** The aggregation of interstellar grains as a result of ballistic collisions produces loosely packed structures with much of their internal volume composed by vacuum (cavities). The molecular material present on the surfaces of the cavities gives rise to a series of reactions induced by cosmic rays, UV radiation, thermal shocks, etc., in high reducing conditions. Thus, a terrestrial type chemistry is given the possibility to evolve inside these cavities. The resulting products are different and of a wider range than those from gas-phase or surface chemistry in molecular clouds. Under conditions similar to those in the aggregate cavities, laboratory experiments have produced amino acids, sugars and other organic compounds from simple precursors. In dense star-forming regions, the molecular species inside aggregates are efficiently shielded against the local UV field. The same molecules were incorporated in the material which formed the Earth, as well as other planets, during the process of its formation and afterwards fell on the surface via comets, meteorites, interstellar dust, etc. This was the source material that can produce, under favorable circumstances, the biopolymers needed for life. The astronomical observations of organic molecules in star-forming regions and the results of analyses of meteorites and cometary dust seem to support the present hypothesis that complex prebiotic molecules form inside dust aggregates and therein survive the journey to planetary systems. The Miller experiment is revisited through innumerable repetitions inside dust grain aggregates.

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**Key words:** interstellar dust aggregates, origin of life, prebiotic molecules.

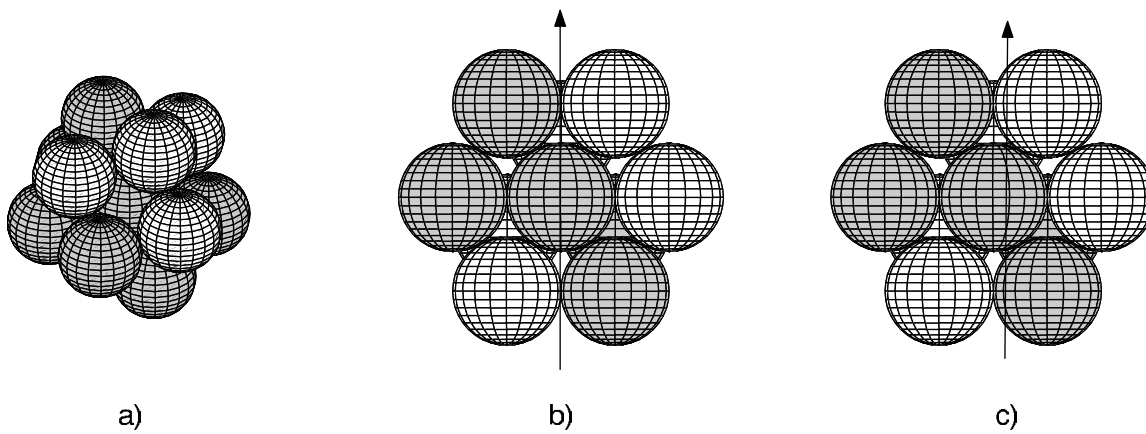
## Introduction

It is well known that the Earth was hit by comets and planetesimals in a massive way until about four billion years ago. These objects most likely retained the prebiotic molecules from the presolar nebula material in their interior and deposited them on our planet. It is the purpose of this work to investigate how organic matter could survive in space and seed planetary systems with the precursor molecules needed for the syntheses of proteins and nucleic acids to make life possible, at least on Earth.

Our study was stimulated by the work of Duley (2000), who noted that the chemistry in grain aggregates presents a completely different scenario with respect to that on the surface of grains or in the gas phase. The analysis of cometary dust (Krueger & Kissel 1989) has shown that, in fact, dust particles, with typical sizes 0.1–10  $\mu\text{m}$ , consist of the aggregation of grains, whose sizes are tens of nanometres. These grains are made of a silicate/carbonaceous core containing

catalytic active metals like Fe, Ni, Zn, Ca, Mg, P, etc. Moreover, in the dense regions of the interstellar medium these inorganic cores acquire an ice mantle of mostly organic molecules (Mathis 1996; Ossenkopf 1993) and, due to collisions, aggregate into fluffy particles (hereafter called aggregates).

Grain surfaces are known to be sites of  $\text{H}_2$  formation and can be responsible for a wide range of reactions involving atoms, molecules and radicals. The resulting species, when exposed to UV radiation, cosmic rays, thermal shocks, etc., are transformed into more complex chemicals. However, in the interior of the aggregates, chemical compounds different from those manufactured on the surface of grains or in the gas phase are likely to be formed. In fact, UV radiation, cosmic rays, thermal shocks, etc., induce a secondary chemistry inside the aggregates where the reaction products cannot escape the cavity. This gives rise to a peculiar situation as chemistry is offered high-temperature, high-density and reducing conditions in the gas phase with rapid quenching of



**Fig. 1.** (a) Adopted shape of the aggregate reference model; (b) wave propagation direction intercepting four points over the aggregate surface; (c) wave propagation direction intercepting six points over the aggregate surface. Darker spheres in (b) and (c) represent carbon-based sub-units while lighter spheres represent silicate-based sub-units.

the reaction products. Furthermore, the molecular species inside the aggregate cavities are partially protected against the destructive effects of the UV radiation (Ehrenfreund *et al.* 2001). The chemical species formed and preserved inside the aggregates eventually become incorporated into the material which condenses when planetary systems are formed. The subsequent infall of comets and planetesimals contributes an additional source of fresh organics. As pointed out by Greenberg & Shen (1999), when grain aggregates are added to a primordial warm bath (local ocean) of sufficient concentration of nutrients, the boundary conditions for non-equilibrium thermodynamics are satisfied (Nicolis & Prigogine 1977) and, therefore, so are the conditions for life to emerge.

The effective production of complex molecules depends on the amount of UV radiation, cosmic rays and heat affecting the aggregates. In this work we model dust aggregates as clusters of spheres covered by ice mantles and with embedded cavities. The UV and cosmic ray doses and collisional heat inside each sphere are computed. The sphere is representative of a sub-unit of the aggregate and is composed of grains clustered around a central cavity. Numerical simulations of the cycling of the aggregates inside and out dense regions are also computed and a plausible scenario is discussed.

### Inside the aggregate cavities

#### *The UV radiation density*

The formation of aggregates by coagulation of grains has been already extensively discussed (Chokshi *et al.* 1993; Ossenkopf 1993; Weidenschilling & Ruzmaiknia 1994; Dominik & Tielens 1997). The timescale for the accretion of volatiles on grains is much faster than that of grain aggregation (Draine 1985), suggesting that the latter process occurs when dust grains have already accreted an ice mantle. During the clustering process substantial vacuum is incorporated into the aggregates producing cavities. The extent of fluffiness depends on the particular host astronomical region

and it is likely to be quite variable. Thus, because of the complexity in morphology and composition, the optical properties of these porous irregularly shaped particles is somewhat different from those of solid homogeneous spheres (Saija *et al.* 2001). To calculate the UV radiation density inside the aggregate cavities we use a numerical technique based on the multipole expansion of the electric field, which has already been tested in treating the scattering of light by arbitrarily shaped, porous, composite particles (Borghese *et al.* 2002).

Grain aggregates are assumed to have the optical properties of Si–Mg–Fe glasses in different proportions mixed with carbonaceous material (Bradley *et al.* 1999). We consider an aggregate reference model consisting of 13 sub-units (spheres) clustered in a round morphology (see Fig. 1(a)). The aggregates have a volume fraction of silicate ( $f_{\text{sil}}$ ) to carbonaceous ( $f_{\text{C}}$ ) material  $f_{\text{sil}}/f_{\text{C}}=6/7$  and a mean size  $D_{\text{agg}}=120$  nm. Since coagulation is likely to occur when dust grains have already accreted an ice mantle, we assume that the sub-units are covered with a layer of condensed molecules (mostly water). The mean radius of the sub-units is  $r_{\text{m}}=20$  nm. The mantle thickness is  $\Delta r=5$  nm, roughly corresponding to 20 monolayers. The resulting ice volume filling factor is  $f_{\text{ice}}\sim 0.5$ . The adopted dielectric constant of silicate and carbonaceous materials are those derived from observations of dusty envelopes around oxygen- (Suh 1999) and carbon-rich (Suh 2000) asymptotic giant branch stars, respectively. The electric constant of the water ice is from Warren (1984).

The random accretion of particles with a distribution in sizes should produce aggregates with internal voids of sizes comparable to those of coagulating particles (Duley 2000). To model the internal voids we assume that each sub-unit has a central cavity of radius  $\rho_{\text{c}}$ . Assuming  $\xi=\rho_{\text{c}}/r_{\text{m}}=0.3, 0.5$  and  $0.7$ , we obtain a vacuum volume fraction of  $V_{\text{V}}\leq 0.35$ , consistent with Mathis (1996). The mean cavity volume is  $L_{\text{V}}\leq 2.5\times 10^{-18}$  cm<sup>3</sup>. The physicochemical parameters of the aggregate reference model are summarized in Table 1.

Table 1. *Physicochemical properties of the aggregate reference model*

Aggregate size	$D_{\text{agg}}$ (nm)	120
Sub-unit size	$2r_{\text{m}}$ (nm)	40
Mantle thickness	$\Delta r$ (nm)	5
Cavity size	$2\rho_{\text{c}}$ (nm)	$\leq 30$
Cavity volume	$L_{\text{V}}$ (cm <sup>3</sup> )	$\leq 2.5 \times 10^{-18}$
Ice fraction	$f_{\text{ice}}$	$\sim 0.5$
Silicate to carbon ratio	$f_{\text{sil}}/f_{\text{C}}$	6/7
Vacuum volume fraction	$V_{\text{V}}$	$\leq 0.35$

We consider an incident plane wave intersecting the aggregate along the directions shown in Figs 1(b) and (c). The wave is linearly polarized normally to the plane of the figure. The assumed line of sight intersects the aggregate in four (Fig. 1(b)) and six (Fig. 1(c)) points, respectively. Using the method after Borghese *et al.* (2002) we compute the radiation energy density  $u_{\nu}$  for the aggregate reference model at the intersection points along the two lines of sight of Figs 1(b) and (c). The results are presented in Figs 2 and 3 for some representative wavelengths. With the definition of the specific intensity  $I_{\nu} = \nu u_{\nu}$  (Ishimaru 1978), where  $\nu$  is the phase velocity, the intensity at the intersection points is given by  $I_{\nu} = T_1(r, \boldsymbol{\eta}) I_{\nu}^*$ , where  $I_{\nu}^*$  is the intensity of the incident field,  $T_1$  is a function of  $r$ , the location on the aggregate surface, and  $\boldsymbol{\eta}$  is the direction of the incident wave.  $T_1$  is completely determined by the shape and the optical properties of the aggregate. For a random dispersion of the grain aggregates,  $T_1$  has then been averaged over the possible directions of propagation of the incident field (Saija *et al.* 2001).

The mean photon density inside any sub-unit of an aggregate is a significant fraction of the incident radiation. In Figs 4 and 5 we show the transmissivity function  $T_2$  for some selected wavelengths as a function of the depth inside spherical silicate and carbonaceous sub-units, respectively. As expected, the radiation density is larger in the voids than in the interstitial material and depends significantly on the size of the vacuum inclusions.  $T_2$  has been then averaged over the volume of the aggregate.

During their lifetime, grain aggregates cycle through several diffuse/dense phases. The history of an aggregate is then tied to the structure of an interstellar cloud complex (Houllahan & Scalo 1992). We describe the complicated evolutionary processes of the journey of an aggregate inside a cloud complex by means of a sequence of pulses of the UV radiation impinging on it. The total lifetime of an aggregate is assumed  $\Delta t_{\text{g}} = 100$  Myr, approximately the average time of a giant molecular cloud (Blitz & Williams 1999). We assume that the number of dense phases is of the order of ten (Sanchez & Parravano 1999) and their life spans are about the free fall time (Spitzer 1978). The initial times of the dense phases are obtained by means of a random generator from the relation

$$P(\bar{t}) = \int_0^{\bar{t}} \theta(t) dt = N \quad (1)$$

where  $t$  is the range  $\Delta t_{\text{g}}$ ,  $\theta(t) = (\Delta t_{\text{g}})^{-1}$  is a probability density function and  $N$  is a random number.

In the diffuse phases of the interstellar clouds, the background UV field  $I_{\nu}^*$  is considered unattenuated, while in the dense phases the external residual field is assumed to be comparable to that internally generated by the cosmic rays (Prasad & Tarafdar 1983; Gredel *et al.* 1989), i.e. approximately 10 000 times less intense than in the diffuse phases (Cecchi-Pestellini & Aiello 1992).

#### Aggregate collisions and cosmic ray impacts

Interstellar aggregates can be impulsively heated by collisions (with other aggregates or grains) and/or cosmic-ray impacts. The time between successive aggregate collisions is approximately given by

$$t_{\text{coll}}/s = 1.67 \times 10^4 \left( \frac{\Delta v_{\text{d}}}{\text{km s}^{-1}} \right)^{-1} \frac{D_{\text{agg}} \rho_{\text{d}}}{m_{\text{H}} n_{\text{gas}}} \quad (2)$$

where  $\rho_{\text{d}}$  is the mass density of the aggregate,  $m_{\text{H}}$  is the atomic hydrogen mass, and  $v_{\text{d}}$  is the root mean square relative velocity given by

$$\Delta v_{\text{d}}/\text{km s}^{-1} = 0.07 \left( \frac{n_{\text{gas}}}{10^4 \text{ cm}^{-3}} \right)^{-1} \left( \frac{D_{\text{agg}}}{200 \text{ nm}} \right)^{1/2} \times \left( \frac{v_{\text{max}}}{\text{km s}^{-1}} \right)^{3/2} \left( \frac{10^{18} \text{ cm}}{l_{\text{max}}} \right)^{1/2} \quad (3)$$

In (3)  $n_{\text{gas}}$  is the gas density, and  $v_{\text{max}}$  and  $l_{\text{max}}$  are the maximum velocity and length scale of the turbulent velocity field (Draine 1985).

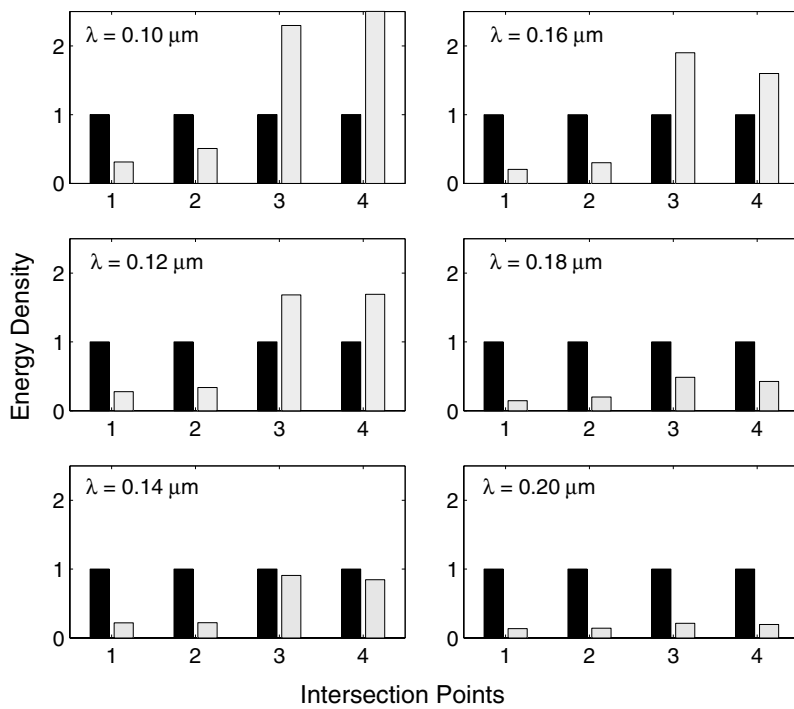
To estimate the cosmic-ray collision time we consider events able to heat aggregates to above 30 K, a temperature excursion covering both classical evaporation and chemical explosions, happening at a rate of  $30 \text{ Myr}^{-1}$  (Léger *et al.* 1985). Cosmic-ray impacts are independent of the dynamical phase and their collision frequency, relevant to the heating, is proportional to the vacuum volume fraction of the aggregate where they produce effectual secondary electrons. Thus, the cosmic-ray collision frequency is  $\nu_{\text{CR}} \sim 30 V_{\text{V}} \text{ Myr}^{-1}$ .

#### Chemical implications

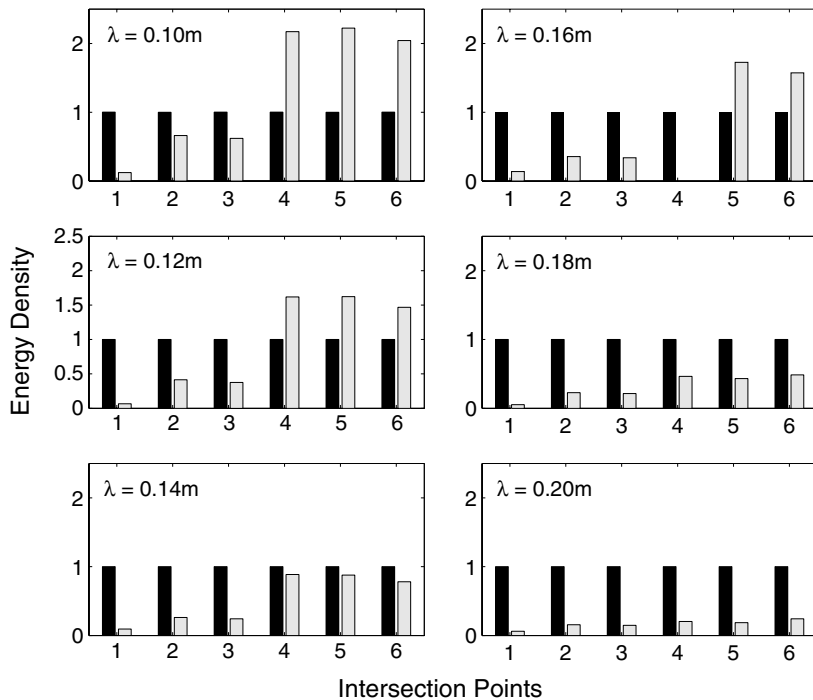
The effective production of complex molecules within grain aggregates depends on the dose of the UV radiation,  $\mathcal{R}_{\tau}$ , impinging on the molecular material contained in a cavity during a period of time  $\tau$

$$\frac{\mathcal{R}_{\tau}}{\langle \sigma_{\text{M}} \rangle} = \int_{\text{UV}} \left\{ \frac{4\pi I_{\nu}^*(t)}{h\nu} \int_{\tau} \langle \langle T_1 \rangle \rangle \times \langle \langle T_2 \rangle \rangle (t) dt \right\} d\nu \quad (4)$$

where  $\langle \sigma_{\text{M}} \rangle$  is the average UV cross section for the species M in Mb ( $1 \text{ Mb} = 10^{-18} \text{ cm}^2$ ). When a cosmic ray collides with an aggregate or after an aggregate collision we consider the composition of the ice cavities *refreshed* by the consequences of the event. This corresponds to setting the dose of the UV radiation absorbed by the mixture inside a



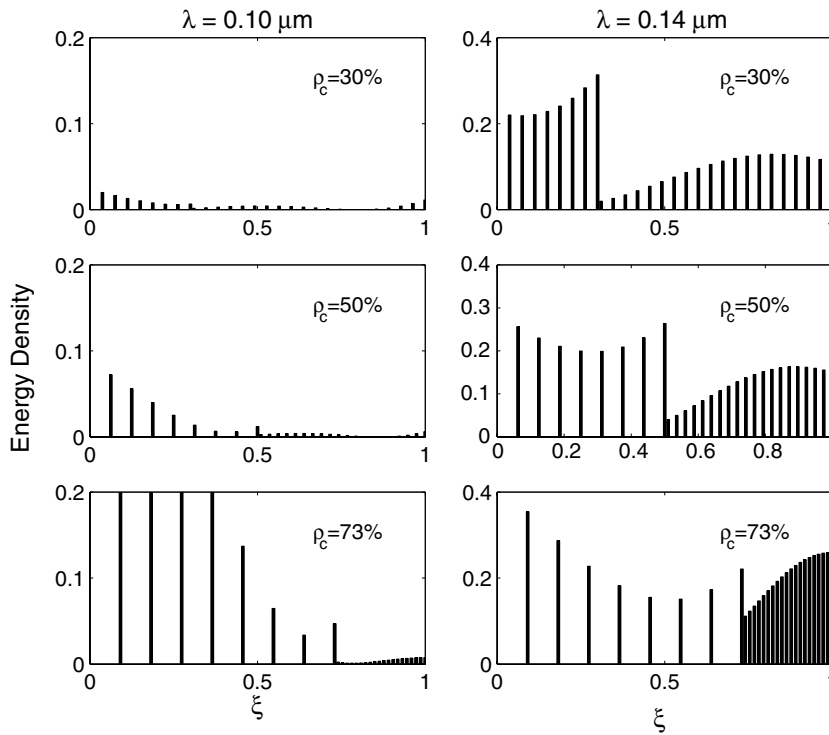
**Fig. 2.** Energy densities at four points on the aggregate surface intercepted by the wave propagation direction depicted in Fig. 1(b). Wavelengths of the incident radiation are reported in each panel. Dark bars indicate the unitary energy of the incoming incident wave.



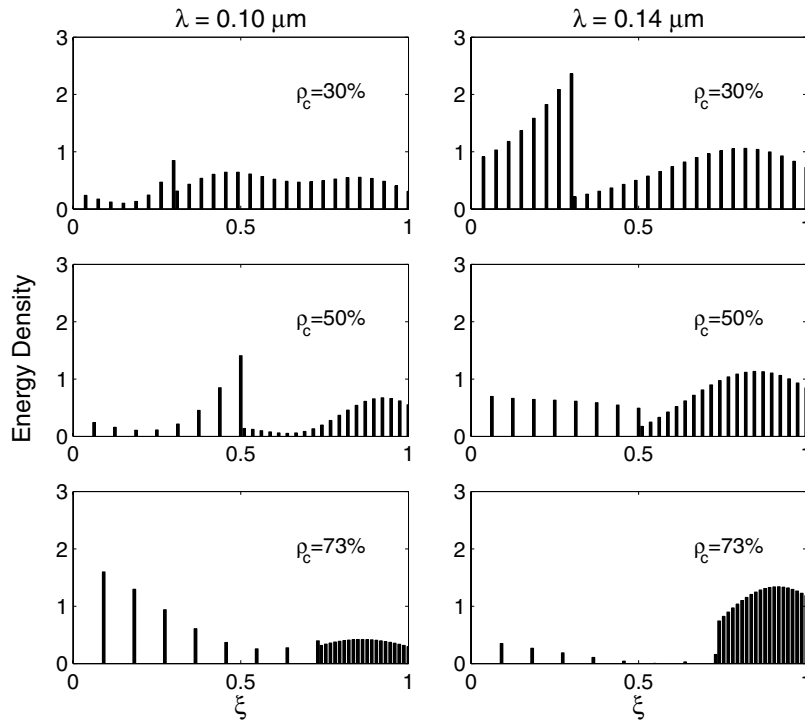
**Fig. 3.** Energy densities at the six points on the aggregate surface intercepted by the wave propagation direction depicted in Fig. 1(c). Wavelengths of the incident radiation are reported in each panel. Dark bars indicate the unitary energy density of the incoming wave.

cavity to zero. Figures 6(a) and (b) show the UV dose absorbed by a molecule with  $\langle\sigma_M\rangle = 1 \text{ Mb}$  located at the center of a sub-unit cavity as a function of the irradiation time  $\tau$ .

The radiation dose  $\mathcal{R}_\tau$  is computed assuming a threshold energy characteristic for the photolysis of the water molecule,  $\sim 6 \text{ eV}$  (Okabe 1978). Interstellar ice inside aggregates is sufficiently photolyzed during its lifetime, absorbing UV



**Fig. 4.** Energy density as a function of the depth in a carbon sub-unit for two selected wavelengths. The size of the inner cavity is indicated in each panel. The incoming energy density is assumed to be unitary.

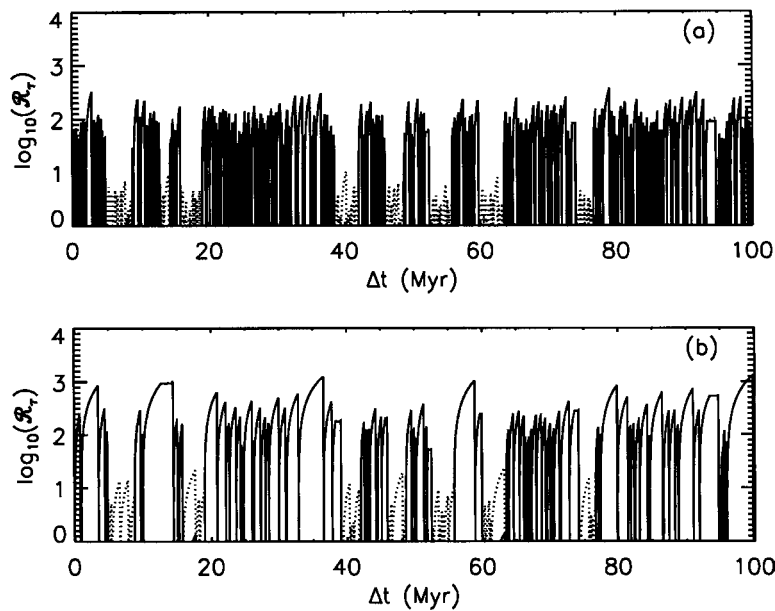


**Fig. 5.** Energy density as a function of the depth in a silicate sub-unit for two selected wavelengths. The size of the inner cavity is indicated in each panel. The incoming energy density is assumed to be unitary.

doses much larger than those absorbed by the ice on the surface of grains. In fact, the latter are only irradiated during the dense phase of their cycle where the UV photon density is small. For convenient comparison with the laboratory results

we derive an average UV irradiation dose

$$\langle \mathcal{R} \rangle = \Delta\tau_g^{-1} \int_{\Delta\tau_g} \mathcal{R}_\tau d\tau \tag{5}$$



**Fig. 6.** UV dose  $\mathcal{R}_\tau$  for a molecule having  $\sigma_M = 1$  Mb as a function of the total irradiation time  $\tau$ . The cavity is located at the center of the aggregate reference model. The assumed vacuum fractions are: (a)  $V_V = 0.35$  (reference model); and (b)  $V_V = 0.05$ .

We obtain  $\langle \mathcal{R} \rangle = 300$  and 2700 for the two cases shown in Fig. 6. Details of the calculation can be found in Cecchi-Pestellini *et al.* (in preparation).

## Chemistry

Laboratory experiments of UV-processing interstellar ice analogues have led to the formation of a non-volatile organic residue (Strazzulla & Baratta 1992; Bernstein *et al.* 1995). The residue consists of a mixture of complex oxygen-rich organic species and is generally dominated by molecules derived from formaldehyde.

As already discussed, dust grain aggregates form a number of cavities in their interior where a peculiar chemistry is likely to occur due to the following reasons: (i) volatile products once formed cannot escape the cavity and accrete on the walls; (ii) the chemistry in cavities benefits from a high UV-irradiation dose ( $\langle \mathcal{R} \rangle \geq 300$ ); (iii) instead of a slow, low-temperature, surface chemistry, a high-temperature, gas-phase chemistry takes place with fast absorption of the reaction products; (iv) densities inside the cavities are terrestrial like,  $n_V \sim \Lambda/L_V \geq \Lambda \times 10^{17} \text{ cm}^{-3}$ ,  $\Lambda$  being the number of molecules injected into the gas phases following a cosmic-ray impact or an aggregate collision; and (v) the atmosphere inside the cavities is hydrogen rich.

These conditions are exactly as Miller (1953) envisaged as plausible for the primitive Earth atmosphere in the famous experiment at the University of Chicago. With his apparatus he succeeded in producing amino acids and other biomolecules starting from simple precursors in a reducing ambient. Grain aggregates represent the interstellar projection of terrestrial micro-labs containing raw materials of reducing

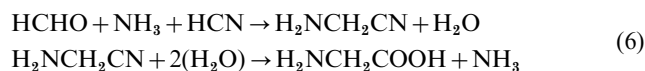
chemical composition suitable for evolution into complex organic species.

The chemistry inside grain aggregates oscillates between two regimes depending on whether the host phase is diffuse or dense. Conditions (i) and (ii) dominate in the diffuse phase. Volatile compounds extracted from the solid mixture by photodegradation re-accrete readily on the cavity ice walls. Aggregate cooling after a heating burst is very effective and the equilibrium temperature is quickly reestablished (Léger *et al.* 1985). Thus, during the time between two subsequent cosmic-ray impacts the chemistry is driven by surface reactions and photodissociation. When a grain aggregate passes through a dense phase, which only produces a mild photolysis, the inner ice mixture may become enriched by a significant number of radicals. After an aggregate collision or a cosmic-ray impact, radicals and molecules from the ice enter a transient, warm (iii), high pressure (iv) gas phase. The final products are likely to be very similar to those obtained from laboratory chemistry under terrestrial conditions. Because of the reducing atmosphere in the cavities (v) large organic molecules are allowed to form, with the inclusion of sputtered atoms from the grain substrate, such as Ca, Mg, Cu, Fe, P, etc. (Kauffman *et al.* 1984; Solov'ev *et al.* 1999). It is recognized that metals are necessary to many important organic constituents of living organisms, such as phosphorus in nucleic acids, copper and iron in blood pigments and magnesium in plant pigments.

The combinations of terrestrial laboratory conditions and the reducing atmosphere inside the aggregate cavities makes it possible the occurrence of a prebiotic chemistry like in the Miller apparatus. The production of sugars, amino acids, bases and other biomolecules is then to be expected, following a terrestrial type chemistry where three body encounters are



highly probable. As an example, the synthesis of amino acid, glycine, is given (Strecker synthesis),



Whenever the grain aggregate undergoes a phase change, the chemical cycle is repeated. If, at some point, the dense phase is star forming, the molecular content inside the aggregates will be able to survive the ambient harsh conditions and eventually seed the newly formed planets with organics.

## Conclusions

The Miller experiment and others that followed, with diverse initial molecules and replacing the electrical discharge with UV light, have shown that under reducing conditions amino acids, sugars and other organic compounds can be produced in a laboratory from simple precursors (Delsemme 1998). On the other hand, these reducing conditions do not seem to have been present on the early Earth. The primary atmosphere, made of hydrogen and hydrogen-rich gases from the solar nebula, was soon lost by the Earth. A secondary atmosphere was brought about mainly by comets and meteorites vaporizing upon impact and consisted of CO<sub>2</sub>, CO and N<sub>2</sub>. In this oxidizing ambient, unfavorable to organic syntheses, the prebiotic molecules contained in the grain aggregates, which formed our planet and subsequently fell on its surface via meteorites and cometary dust, could have been the source material to produce the biopolymers needed for life. In this scenario, the production of biopolymers is restricted to those sites that offered the right conditions for the chemistry to occur.

Many of the prebiotic compounds generated in various laboratory experiments have also been detected in carbonaceous meteorites. Furthermore, the family of small precursor molecules (H<sub>2</sub>O, HCN, HCHO, HCCH, etc.) used in laboratory syntheses of complex species are abundant in molecular clouds. This evidence supports the hypothesis that complex prebiotic molecules are formed in the dust aggregates and therein survive the journey from the interstellar medium to planetary systems.

If life did originate on the surface of Earth, then it either could have succeeded many times before the end of the major impact era (3.8 billions years ago) or, if it started only after the conditions became less hostile, it happened rather quickly. In either hypothesis, grain aggregates are an ideal factory (stable and reducing environment) for the ingredients needed to start life early and quickly.

## Acknowledgement

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## References

- Bernstein, M.P., Sandford, S.A., Allamandola, L.J., Chang, S. & Scharberg, M.A. (1995). *Astrophys. J.* **454**, 327–344.
- Blitz, L. & Williams, J.P. (1999). *The Origin of Stars and Planetary Systems*, eds Lada, C.J. & Kylafis, N.D., pp. 3–28. Kluwer Academic, Dordrecht.
- Borghese, F., Denti, P. & Saija, R. (2002). *Scattering by Model Nonspherical particles*. Springer, Heidelberg.
- Bradley, J.P. *et al.* (1999). *Science* **285**, 1716–1718.
- Cecchi-Pestellini, C. & Aiello, S. (1992). *Mon. Not. R. Astron. Soc.* **258**, 125–133.
- Chokshi, A., Tielens, A.G.G.M. & Hollembach, D. (1993). *Astrophys. J.* **407**, 806–819.
- Delsemme, A. (1998). *Our Cosmic Origins*, pp. 145–146. Cambridge University Press, Cambridge.
- Dominik, C. & Tielens, A.G.G.M. (1997). *Astrophys. J.* **480**, 647–673.
- Draine, B.T. (1985). *Protostars and Planets II*, eds Black, D.C. & Mathews, M.S., pp. 621–640. University of Arizona Press, Tucson, AZ.
- Duley, W.W. (2000). *Mon. Not. R. Astron. Soc.* **319**, 791–796.
- Ehrenfreund, P., Bernstein, M.P., Dworkin, J.P., Sandford, S.A. & Allamandola, L.J. (2001). *Astrophys. J.* **550**, L95–L99.
- Gredel, R., Lepp, S., Dalgarno, A. & Herbst E. (1989). *Astrophys. J.* **347**, 289–293.
- Greenberg, J.M. & Shen, C. (1999). *Astrophys. Space Science* **269**, 33–55.
- Houllahan, P. & Scalo, J. (1992). *Astrophys. J.* **393**, 172–187.
- Ishimaru, A. (1978). *Wave Propagation and Scattering in Random Media*. Academic Press, New York.
- Kauffman, J.W., Hauge, R.H. & Margrave, J.L. (1984). *High Temp. Sci.* **18**, 97–136.
- Krueger, F.R. & Kissel, J. (1989). *Origins Life* **19**, 87–93.
- Léger, A., Jura, M. & Omont, A. (1985). *Astron. Astrophys.* **144**, 147–160.
- Mathis, J.S. (1996). *Astrophys. J.* **472**, 643–655.
- Miller, S.L. (1953). *Science* **117**, 528–529.
- Nicolis, G. & Prigogine, I. (1977). *Self-organization in Non Equilibrium Systems*. John Wiley & Sons, New York.
- Okabe, H. (1978). *Photochemistry of Small Molecules*. John Wiley & Sons, New York.
- Ossenkopf, V. (1993). *Astron. Astrophys.* **280**, 617–646.
- Prasad, S.S. & Tarafdar, S.P. (1983). *Astrophys. J.* **267**, 603–609.
- Saija, R., Iati, M.A., Borghese, F., Denti, P., Aiello, S. & Cecchi-Pestellini, C. (2001). *Astrophys. J.* **559**, 993–1004.
- Sanchez, N.M. & Parravano, A. (1999). *Astrophys. J.* **510**, 795–805.
- Solov'ev, V.N., Polikarpov, E.V., Nemukhin, A.V. & Sergeev, G.B. (1999). *J. Phys. Chem. A* **103**, 1984–1994.
- Spitzer, L.S. (1978). *Physical Processes in the Interstellar Medium*. Wiley, New York.
- Strazzulla, G. & Baratta, G.A. (1992). *Astron. Astrophys.* **266**, 434–438.
- Suh, K.-W. (1999). *Mon. Not. R. Astron. Soc.* **304**, 389–405.
- Suh, K.-W. (2000). *Mon. Not. R. Astron. Soc.* **315**, 740–750.
- Warren, S.G. (1984). *Appl. Opt.* **23**, 1206–1225.
- Weidenschilling, S.J. & Ruzmaikina, T.V. (1994). *Astrophys. J.* **430**, 713–726.