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# Chiral Selection in Space: Role of Cosmic Dust

**Abstract** – It is well known that the amino acids occurring in proteins (natural amino acids) are exclusively of L-configuration. Among the many scenarios put forward to explain the origin of this chiral homogeneity, one involves the asymmetric photolysis of amino acids present in space, triggered by circularly polarized ultraviolet radiation. Here, I propose that amino acids formed in the cavities of dust aggregates in protoplanetary discs are exposed to asymmetric photolysis induced by an effective ultraviolet circularly polarization generated in situ.

## 1. *Introduction*

The origin of homochirality of amino acids and sugars is so far an unfilled gap for the theories of the chemical origin of life. Why amino acids occurring in proteins are, almost exclusively, of L-conformation and only D-conformation sugars enter the RNA and DNA molecules is, in fact, the most crucial question to be answered before indulging in any chemical, biological or philosophical discussion on the origin of life.

Quantitative analyses of cosmic debris show some amino acids presenting an excess of the L-conformation enantiomer (e.g., Engel & Nagy 1982), while both rare and common sugar monoacids (aldonic acids) may contain significant excesses of the D-enantiomer (Cooper & Rios 2016) in straightforward similarity with terrestrial biomolecular homochirality. This coincidence is too striking to be fortuitous; it points out that products of routine cosmic chemistry contributed to the early Earth organic pool and facilitated prebiotic molecular evolution.

Several controversial theories have been developed to explain an abiogenic origin of the chiral homogeneity in terms of the physico-chemical processes involved.

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For evident reasons, the highest astrophysical relevance has been awarded to processes involving radiation and magnetic fields. Among photochemical effects, only Circularly Polarized Light (CPL) and a static magnetic field collinear with a light beam are truly chiral systems and thus can potentially produce an enantiomeric enhancement within initially racemic mixtures.

The interaction of CPL with an isotropic medium containing chiral molecules in the presence of a constant external magnetic field may be described by several phenomenological constants, relating to optical activity and dichroism, summarized by slightly different dielectric constants associated with right- and left-handed CPL (e.g., Jorissen & Cerf 2002).

In this work I propose a new scenario in which amino acids formed in the cavities of dust grain aggregates (Duley, 2000, Williams & Cecchi-Pestellini 2016) in protoplanetary discs, are exposed to asymmetric photolysis induced by an effective ultraviolet CPL generated *in situ*. The enantiomeric excess of chiral biomolecules produced and protected in the cavities of grain aggregates may have contributed to the early Earth organic pool and facilitated prebiotic molecular evolution.

## 2. *The possible role of cosmic dust in the emergence of life on Earth*

Only a very small fraction of the organic compounds in nature are found in planets or comets and other condensed objects. By far the larger quantity – more than 99.9% by mass – reside in the enormous molecular clouds in interstellar space of the Milky Way and other spiral galaxies. Abiotic organic chemistry, as observed in molecular clouds, offers a glimpse of the chemical evolution preceding the onset of life on our own planet, and allows us to evaluate the possibility that, during the evolution from a molecular cloud to a planetary system, complex organic molecules are formed, transformed and preserved until they are incorporated into comets and meteorites.

Do complex organic molecules survive the processes of star and planet formation? The formation of a planetary system is a violent event, so the intricate chemical history of the gas from which the planet forms may be obliterated, requiring chemical evolution to be continuously restarted. On the other hand, the chemical mechanisms that generate biomolecules in space could be transferred to newly formed planets during a bombardment phase by the dust grains aggregates, comets, asteroids, and meteorites, so there is a potential connection between prebiotic organic chemistry and the chemistry of the interstellar medium. These exogenous products could, of course, have been complemented by substances arising on Earth.

Cosmic dust may have contributed to the emergence of life on Earth many times during the long evolutionary pathway that eventually gave rise to our planetary system, in the following ways: (1) contributing precursors for prebiotic chemistry in larger bodies, (2) serving as building blocks from which future comets, asteroids, and other celestial bodies may originate, (3) inducing the formation of the Earth itself and – more generally – planets, (4) delivering complex organic molecules to the early Earth and Mars during the late heavy bombardment 4.5 billion years ago, (5) providing a stable and reducing environment for the ingredients needed to start life early and quickly, and (6) contributing to chiral selection in space. While there is considerable agreement regarding the points from (1) to (4), the last two issues are rather speculative and no general, or even partial consensus on the production and selection of chiral organic molecules in protoplanetary discs has been reached. The present proposal is based on these last two hypotheses.

### 3. *The potential of ice cavity gas-phase chemistry for chemical complexity*

All the early speculations about the origins of life on Earth were based on Solar System processes. Of these speculations, the more influential were the suggestions of possible Miller–Urey type syntheses in a reducing planet atmosphere, following production and recombination of radicals, and of catalytic, Fisher–Tropsch type processes in the early stages of the solar nebula. In 1957 Miller showed that formaldehyde and hydrogen cyanide were key intermediates in the synthesis of glycine. This led Orò. and his co-workers (1961) to study the products of a solution of ammonium cyanide ($NH_4CN$) in water, discovering that $NH_4CN$ was converted in adenine, one of the four bases of DNA. Such, and other similar, discoveries determined the direction of research on prebiotic chemistry for many years. However, our understanding of the atmosphere on early Earth has changed since then, and it is now believed that the atmosphere consisted mostly of carbon dioxide, nitrogen, and water. Under such conditions, prebiotic molecules are produced only in trace amounts.

However, in the complex process leading to the formation of circumstellar discs around young stars from prestellar dense molecular clouds, physical conditions similar to those envisaged in the early prebiotic experiments may arise. In the high densities of the discs, these ice-coated dust grains collisionally agglomerate, assembling in loosely packed structures with much of their internal volume being vacuum and trapped ices. Sputtering of silicate, carbon solids, and PAHs by cosmic-rays will inject heavier atoms, ions and molecules into these ices.

The timescale for the accretion of volatiles on grains is much faster than that of grain aggregation, implying that the latter process occurs when dust grains have already accreted ice mantles. Interstitial voids must occur even in highly organized, densely packed structures. For example, dense packing of like spheres in a face-centered cubic lattice leaves 26% of space unoccupied. In surface chemistry the time delay between the adsorption and reaction steps may be substantial if the reaction products are non-volatile, but they can be short for prompt reactions. The products of surface reactions are either retained on dust or desorbed to the ambient gas. Duley (2000) noted that the interior of dust aggregates offers a different intermediate possibility: the re-accretion of reaction products by other components of the aggregate. This re-deposition may occur on the surface of other dust particles or on components of an ice mantle. As desorbed products can be in an energetic state, these secondary reactions might be expected to mimic some aspects of high-temperature chemistry. Aggregate grains bring together all components of the interstellar gas and dust, a unique situation, outside planetary systems. As reaction products can remain trapped within aggregates and are shielded from radiation, conditions exist for the formation of larger molecules. The feedstock for this chemistry would be the ices accumulated during aggregation, together with light atoms and radicals from the ambient gas that diffuse into the interior of the aggregate.

Dust aggregates can be impulsively heated by collisions with other aggregates or grains and by cosmic-ray impacts. The heat released during a collision may lead to the vaporization of the ice content filling the cavities, in which radicals and molecules from the ice enter a transient, warm, high pressure gas phase, giving rise to: (1) a solid-state chemistry involving elements such as Si, Mg and Fe sputtered from silicate particles; (2) facilitated secondary reactions and rapid quenching of the reaction products; (3) a hydrogen rich atmosphere inside the cavities. The resulting mixture is a reasonable analogue of the conditions that Stanley Miller supposed as plausible for the primitive Earth atmosphere. Therefore, grain aggregates may represent in the interstellar medium the equivalent of terrestrial micro-laboratories containing raw materials of reducing chemical composition suitable for conversion into complex organic molecules. 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 large organic molecules are allowed to form. Recent numerical experiments (Saitta & Saija 2014) based on ab-initio molecular dynamics simulations of aqueous systems subject to electric fields (e.g. describing lightning) and on metadynamics analysis of chemical reactions showed that glycine spontaneously forms from mixtures of simple molecules. Formic acid and formamide are key intermediate products of the early steps of the Miller reactions. Formamide represents the simplest molecule containing the peptide bond. It is therefore of great interest as an important precursor in the abiotic synthesis of amino acids, and of further prebiotic chemistry. Remarkably, when nitrogen compounds are present in the initial mixture, the processing of interstellar ice analogues produces formamide (e.g., Jones *et al.* 2011), and under suitable conditions aminoacids (e.g., Muñoz-Caro *et al.* 2002), and sugars (de Marcellus *et al.* 2015).

## 4. *Chiral selection in protoplanetary discs*

The formation yield of complex molecules depends critically on the dose of ultraviolet radiation impinging on the molecular material. Cecchi-Pestellini *et al.* 2005 showed that the interiors of grain aggregates are, in fact illuminated by a substantial fraction of the incident radiation. In addition to implications for the photochemistry of icy mixtures trapped in aggregate cavities, such residual radiation acquires polarization properties, that are directly related to asymmetric photo-reactions of chiral molecules.

The most general state of polarization of an electromagnetic field is elliptic and the direction of propagation is given by the Poynting vector $\boldsymbol{S}$. The latter has a fixed direction for a plane homogeneous wave and/or for a scattered field in the far zone. In both these cases the plane of polarization ellipse is orthogonal to the Poynting vector, so that the state of polarization is conveniently described by the Stokes parameters constructed with the components of the field orthogonal to the direction of propagation. In the interstitial material and in the cavities of the aggregate the direction of propagation of the field changes from point to point. The plane of polarization ellipse is in general not orthogonal to the vector $\boldsymbol{S}$. Consequently, the state of polarization of the field cannot be described by the usual Stokes parameters but it needs a more general description (Carozzi *et al.* 2000), e.g., through the definition of the real vector $\boldsymbol{V} = i\,(\boldsymbol{E} \times \boldsymbol{E}^*)$, where $\boldsymbol{E}$ is the electric field and $\boldsymbol{E}^*$ is its complex conjugate. The magnitude of $\boldsymbol{V}$ is $2/\pi$ times the area of the polarization ellipse. When $\boldsymbol{V} = 0$ the field is linearly polarized, otherwise the electric field rotates, as a function of time, in a counterclockwise sense with respect to $\boldsymbol{V}$. As a consequence, the sign of $V_S = \boldsymbol{V}\boldsymbol{S}/|\boldsymbol{S}|$ gives the sense of field rotation with respect to the direction of propagation of the electromagnetic energy. The components of the vector $\boldsymbol{V}$ are found expanding the spectral density tensor (the representation of the coherency dyad $\rho = \boldsymbol{E} \otimes \boldsymbol{E}^*$ in rectangular coordinates) in terms of the unit matrix $\mathbf{1}_3$ and of the eight Gell-Mann matrices that are the generators of the group SU(3). Details on the generalized description of the polarization of electromagnetic waves can be found in Borghese *et al.* 2005.

This has interesting consequences, e.g., when a linearly polarized wave impacts on the aggregate, the net result is the creation of additional components of the fields that thus lose their original state of being linearly polarized, acquiring a degree of circularity. In other words, the field depolarizes (becomes elliptically polarized) in the inner cavities of the aggregate giving rise to CPL, and thus providing a photo-selective mechanism.

### 4.1 *A proof of concept*

I approximate the aggregate with a simple model consisting of a homogeneous sphere with radius $\rho_0$ embedding a spherical cavity with radius $\rho_c$. The incident field is assumed to propagate along the $z$ axis and the reference plane is chosen to be the $x$-$y$ plane (Fig. 1a). The location of the embedded cavity is determined by the couple of polar angles $\theta_c$ and $\varphi_c$, and by the distance from the center of the host sphere. I consider host spheres with radii around the value $\rho_0 = 100$ nm, taken as a reference. Dust particles of these sizes are efficient in causing interstellar extinction at visual wavelength. I choose four candidates for the interstitial material, namely silicates, amorphous carbon, water ice, and a Bruggeman mixture (Bohren & Huffman 1983) of 30% silicates, 30% amorphous carbon and 40% water ice. The Bruggeman mixing rule is applied only to the interstitial material, whereas the cavity is treated as a separate entity.

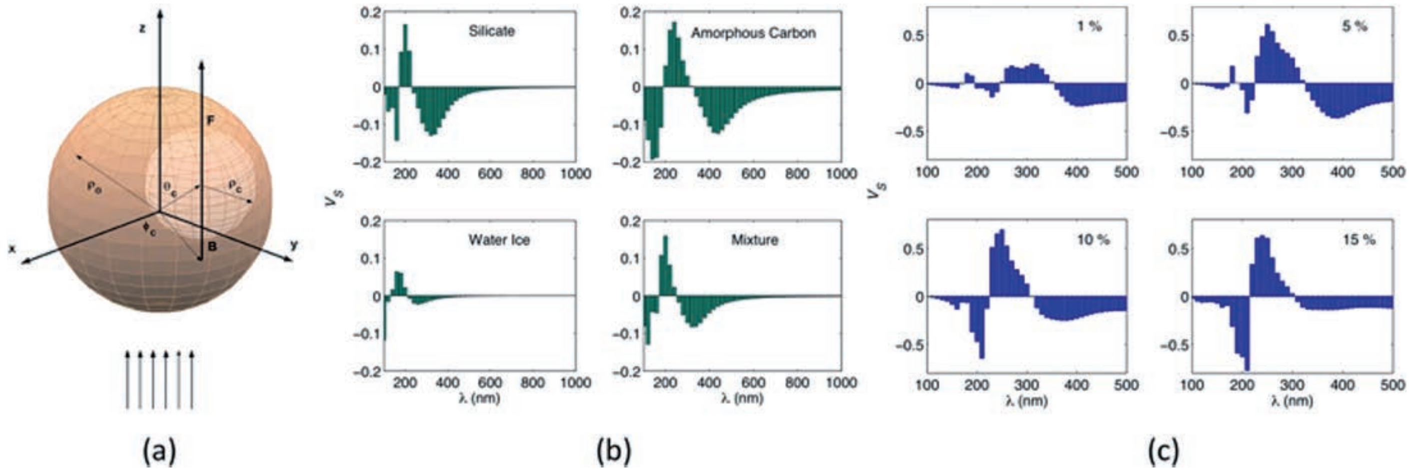


Fig. 1. (a) geometry of the interaction between the impinging wave and the «aggregate»; (b) $V_S$ computed at the point B as a function of the wavelength for a aggregate and cavity radii of 100 and 74 nm (40% in volume), respectively, using different dust materials; (c) same as in (b) but with the variable cavity size; the dust material is the Bruggeman mixture.

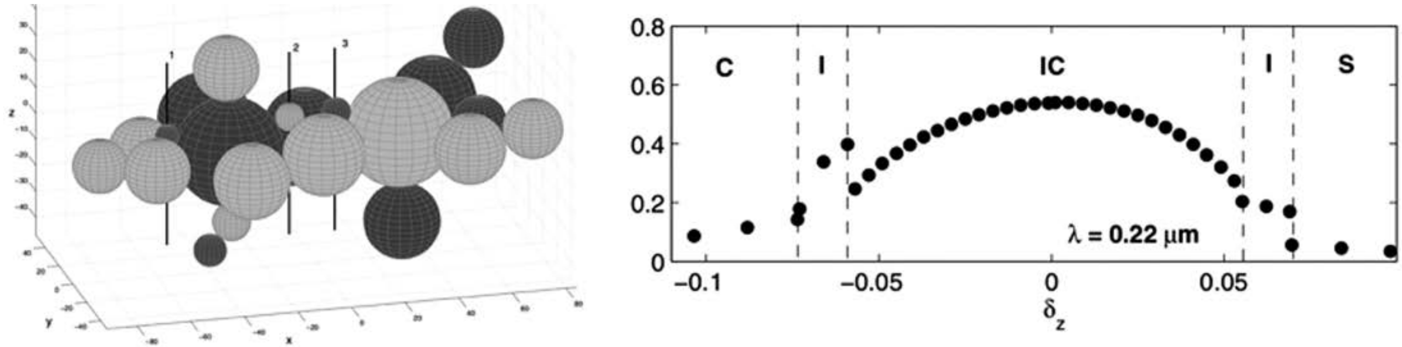


Fig. 2. Left panel – Geometry of the aggregate of spheres of different radii. The darker spheres have a core of carbon, whereas the lighter ones have a core of silicates. All the spheres are covered by a mantle of water ice whose thickness is 25% of the corresponding radius. Vertical lines indicate the position of resulting interstitial cavities; Right panel – $V_S$ within cavity 2 as a function of the penetration of the radiation into the aggregate, for incidence along the z axis and polarization along the x axis. $\delta_z$ is the z coordinate scaled by the size of the aggregate. S: silicate sphere; I: ice layer; IC: interstitial cavity; C: carbon sphere.

$V_S$ is computed at B and F (see Fig. 1a), i.e. the points at which the parallel to the *z* axis through the center of the cavity crosses its surface. Calculations show that: the largest depolarization effects occur for cavities tangent to the surface of the host sphere; rotating the position of the cavity with respect to both the *x* and *y* axes the sign of $V_S$ is unchanged; the depolarization appears to be almost independent of the refractive index, the maximum value of $V_S$ occurring in the range 100 – 500 nm for any choice of the material, while no depolarization occurs above 1 μm; depolarization effects are only slightly dependent on the volume of the embedded cavity (Fig. 1c); for evident symmetry reasons the field does not depolarize at points B and F when the cavity is centered on the *z* axis; the sign of field rotation alternates with wavelength (Fig. 1b).

This last property is particularly intriguing. In fact, every proposed mechanism for asymmetric photolysis induced by an external source of ultraviolet CPL has to meet with the Kuhn-Condon rule (e.g., Mason 2000). The most effective proposed external ultraviolet CPL sources operate only at a single photochemically active circular dichroic band, which is not shared by all biogenic amino acids. (Cerf & Jorissen 2000). In the present model the CPL, that spans a wide wavelength region from 100 nm to 1 μm, for volumes of the embedded cavity larger than the 5% of the volume of the host sphere, changes twice the sense of field rotation at approximately 200 and 300~nm. The inversion at 200 nm which fits exactly the circular dichroic spectra of Tryptophan and Proline occurs, for instance in an aggregate with radius $\rho_0 = 150$ nm, embedding a cavity with a volume about 40% of the volume of the host sphere.

### 4.2 *A more realistic case*

As a natural extension of the synthetic aggregate presented in the previous paragraph, dust grains are modelled here as a fluffily substructured collection of 25 stratified spheres, composed by a solid refractory core (silicates or amorphous carbon) covered by an icy water mantle (Fig. 2, left panel). The radii of the subunits are randomly chosen. Such a model includes the presence of interstitial voids generated by coagulation of particles.

A more realistic aggregate allows the possibility to assess the presence of trends and regularities in the wave depolarization pattern. $V_S$ is computed at several points within the cavities for incidence along all coordinate axes (which is equivalent to a rotation of the target grain), in the wavelength range from 0.1 to 0.3 μm. The results indicate that a much lower depolarization occurs for incidence along the *x* axis, as well as along the *y* axis. Generally, the sign of $V_S$ changes for rotations of the aggregate with respect to a fixed direction of incidence and of polarization.

Major results of the study are as follows: (1) in all examined cases a net depolarization is present; (2) depolarization in a given cavity depends exclusively on the environment, i.e., morphology and chemical composition of the aggregate close to the cavity; (3) any time there is significant depolarization in an interstitial cavity, a significant amount occurs in its icy boundaries (see Fig. 2, right panel), the most interesting region for photochemistry; (4) in all examined cases, the depolarization depends on the wavelength, with $V_S$ varying both in sign and/or in value, in going from λ = 0. 1 to 0.2 μm; (5) significant depolarization occurs when the projected section of the target aggregate on a plane perpendicular to the direction of incidence of the wave bears enough asymmetry; (6) the sign of $V_S$ changes erratically from cavity to cavity; there is however a tendency of CPL sign to be the different in the inner and outer parts of the aggregate; (7) rotations can affect the sign of Vs, but, on average, a net depolarization of a given sign is always present, i.e., the integral of $V_S$ over the rotation angle is never zero; (8) the depolarization appears to be essentially determined by the geometry of the nearest environment.

Since the sign of $V_S$ is not the same in different cavities of the same aggregate, it is not clear whether or not the depolarization, i.e., the presence of an effective CPL within the ice layers, might be relevant to the selection of chiral molecules.

## 5. *Discussion and conclusions*

In this work, I address the problem of field depolarization within interstellar dust aggregates, in which coagulation generates interstitial cavities partly filled with icy condensed gas. The present calculations show that a net depolarization effect is always present in all cavities, although the signs of generated CPL depend on the location within the aggregate in an unclear way. This prevents the establishment of a net enantiomeric excess of a given symmetry.

Since the effect is purely geometric, it is not chiral since it does not provide a symmetry breaking. In fact, the sign of the induced circular polarization changes with rotation of the cavities with respect to axes parallel to the propagation of the wave. The breaking of spatial symmetry may be provided by dust grain alignment with respect to the stellar incident field. When embedded in a protoplanetary disc, real aggregates can be efficiently aligned by interacting with the gaseous flow both in subsonic and supersonic regimes. The alignment arises from grains having irregularities that scatter atoms with different efficiency in the right and left directions. Although, the tendency for grains is to align with long axes perpendicular to the magnetic field, paramagnetic dissipation is not involved (Lazarian & Hoang 2007), and the specific chemical composition of a dust aggregate is irrelevant. In conclusion, if the aggregates in the protoplanetary disc are aligned, they must share the same geometrical asymmetry: the denser part leading and the more porous one following. Because the more porous part has more cavities a net enantiomeric excess of chiral biomolecules is to be expected in the aggregates.

The ubiquitous mutual presence of ultraviolet linearly polarized radiation and dust aggregation in star forming regions may provide the conditions for a widespread universal replication of the chiral selection.

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