Astrochemistry and Astrobiology over the last 20 years

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Abstract

A review of the achievements of astrochemistry and astrobiology over the past 20 years is given. Advances in astrochemistry in understanding the processes of emergence and survival high molecular weight chemical compounds are directly related to the conditions of prebiomolecules origin, like -amino acids and complex hydrocarbons. And if on the case of amino acids and hydrocarbons synthesis , the astrophysical picture seems quite clear, then on the case of the emergence of chiral amino acids, of which the proteins of living organisms are composed, there is no generally accepted point of view. Probably they occurred in certain photochemical transformations under the influence of circularly polarized radiation in the conditions of star formation regions of molecular clouds.

Keywords: *astrochemistry, astrobiology, complex molecules, irradiation, molecules suvervability under hard radiation, origin of life*

1. Introduction

1.1. Content

1. About astrochemistry
2. Dust particles and origin of complex species
3. On astrobiology
4. Life in expanding Universe
5. Conclusion

1.2. Astrobiology, astrochemistry and all that - list of clarifying definitions

Astrochemistry is the science (as a part of astrophysics) about the origin and existence of chemical compounds in the Universe, including dust grains. Dust plays a particularly important role in the formation of molecules and more complex ones, in general, and in elementary processes in physics and chemistry of molecular clouds, in particular. Interstellar dust consists of particles of graphite or silicates 0.05-1 μ in size, which may have ice mantles (H_2O, CO, CH_4...) an order of magnitude larger. Astrobiology is mainly concerned with the origin of prebiomolecules (amino acids, complex hydrocarbons, sugars, etc.) and their survival, from the point of view of the only form of terrestrial life as we know it.

It should be highlighted now that since discovery of helium in the solar spectrum in 1868 astrophysics was based essentially on theory of atoms (and ions). A good example is the book of S. Rosseland, 1931, Astrophysics - on the base of atomic theory (Astrophysik: Auf Atomtheoretischer Grundlage) Rosseland (1931).

Ambartsumyan's article of 1933 should also be mentioned Ambarzumian (1933) (concerning again with atoms and ions), by the way one of the first related to the study of the physics of the interstellar medium.

After 100 years, however, the successes of observational astrophysics are associated primarily with molecular astrophysics Shaw (2022). By early 2024, more than 256 molecules had already been observed in the Universe (without isotopic differences). Also part of molecules are identified in circumstellar disks around newborn stars.

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It is clear that today to study astrobiology, at first, prebiomolecules (that is large and very large chemical compounds), it is necessary to use theoretical and observational methods of Molecular astrophysics, which is obviously known as Astrochemistry.

Important molecules like H_2, CO, H_2O, CO_2, NH_3, CH_4, H_2CO, CH_3OH,...etc. usually origin and survive inside of molecular clouds in star-formation regions Shaw (2022). Also PAH (polycyclic aromatic hydrocarbons, for example, $C_{24}H_{12}$ - coronene), fullerens (C_{60}), aminoacids, shugars, alcohols etc. are observed in such regions. Corresponding timescales are quite appropriate: if ages of star-formation regions are a few millions years, while dust and ice covers of grains origin in dense environment of protostellar clouds for only a few thousands - a few ten thousands years.

There is one contradiction to standard picture that dust is originated in dense cold outflows of AGB stars with masses less than 8 solar, and in supernovae explosion. The case is that due to supernovae only silicate dust is arrived, while graphite dust is originated in AGB phase for which 1-2 billions years are necessary. On the other hand, PAHs molecules, for which graphite is necessary, were detected in the farthest galaxy SPT0418-47 in 2023 by James Webb Space Telescope Spilker et al. (2023). That galaxy is 12.3 billion years old, and we note the problem concerning with the modern estimate of the Universe age, 13.8±0.2 billions years. So PAH couldn't have time to origin. Also survivability of PAHs under hard conditions of early Universe should be taken into account, to have balance between originated and destroyed molecules, PAH is connected with graphite, which is created in AGB stars with C/O>1 in 1.5 b.y. The following explanation is that probably such a dust was originated via binary carbon-enhanced metal-poor like stars, or specific single AGB in such a shortened time concerning conditions of first generation of stars.
At last but not least the most important thing is a homochirality of pre-biomolecules, aminoacids, heavy hydrocarbons etc. Meierhenrich (2008). That is, proteins of Earth living organisms (and any other molecular complexes with asymmetric C-atom) consist of only L - "aminoacids" (L - alanine etc). But homochirality of such molecules couldn't be originated on Earth ! This is the most important conclusion of last 20-30 years and this is a reason to include astrophysics into the common picture !

2. Important dates concerning origin of life on Earth

The Sun was formed 4.6±0.1 billion years ago, the Earth a little later, 4.54±0.05 billion years ago **?**. Heavy bombardment of the Earth by giant comets and asteroids has ceased 3.8 b.y. ago. They have delivered primary atmosphere and (partly) water of oceans. The oldest sedimentary rocks of the Earth date back to 3.8 b.y. ago. First traces of life on Earth have found 3.8 b.y. ago. First blue-green algae in oceans have arrived 2.7 b.y. ago. Atmospheric oxygen with relative abundance larger than 1 % has age 2.4 b.y.

Currently known is that the origin of life on Earth was preceded by a period of chemical complexity of molecular compounds outside the Earth. In the amino acids of proteins of living organisms, molecular symmetry is broken; only their left-handed forms exist Meierhenrich (2008). The laws of heredity of self-reproducing systems representing terrestrial life forms are implemented through the "genetic code", the structure of the components of which significantly depends on the presence of chirality, because exactly a sequence of nucleotide triplets in nucleic acids determine the corresponding order of amino acids in a protein structure. The origin of such amino acids on Earth with broken chiral symmetry has been ruled out due to the lack of suitable physical agents to induce their synthesis, such as circularly polarized light with photon energies in the range of 6-12 eV. At the same time, the sources of such radiation in star formation regions are known, and were quite capable of causing their genesis. Other forms of chiral synthesis are much less efficient, on the order of many magnitudes.

Now let us list 5 steps that are obviously necessary for the emergence of the known form of life (on Earth).
1. Origin of molecules - (H_2 etc.).
2. Dust particles and their ice mantles (with sizes about 0.01-0.3 μ).
3. Molecules chemical complexisation.
4. Origin of prebiomolecules (separation from environment by membranes).
5. Chiralization - proteins of terrestrial living organisms are product of polymerisation of only left-handed amino-acids.

Let's discuss these steps separately.

1. Origin of molecules, beginning with chemistry of simple molecules, (H_2 etc.). Molecules are synthesized either in gaseous or in the solid form, and hydrogen efficiently form on the surface of dust particles Shaw

(2022). In star formation regions (SFR) of Molecular Clouds behind the photodissotiation regions (PDR) H_2 may originate on dust grain surfaces (that is not in gas-phase) with time-scale

$$t(H_2) = 1.5 \cdot 10^9/n \text{ yr}, \quad (1)$$

that is for SFR density of $n \geq 10^6$ cm^{-3}, $t(H_2) \leq 1500$ yr. Characteristic time-scale t(PD) for a H_2 photo-dissociation in the typical unshielded region of the ISM, for standard UV radiation measure and without other sources present would be in the range of 33-3300 years.

As is mentioned above 256 molecules are observed in the ISM till 2024. The most important are H_2, CO, CO_2, H_2O, NH_3, CH_4, H_2CO, HCN, CH_3OH etc. and their ions (up to $HC_{11}N$ and PAH, like $C_{24}H_{12}$, and even fullerens C_{60} and C_{70}).

2. Dust particles and their ice mantles.

Dust grains come now with supernovae (SN) ejections and asymptothic giant branch (AGB) star winds. Initial sizes of graphite grain (AGB) and silicate (SN) cores are about 0.01 μ and icy mantles grow up to sizes of about 0.1 μ. Time-scale for dust growth in a dense cold medium of SFR is

$$t(\text{mantle}) = 3.0 \cdot 10^9/n \text{ yr}. \quad (2)$$

Rapid growth in the SFR with $n \geq 10^6$ cm^{-3} gives $t \sim 10^3$ years at $T \sim 10-20$ K.

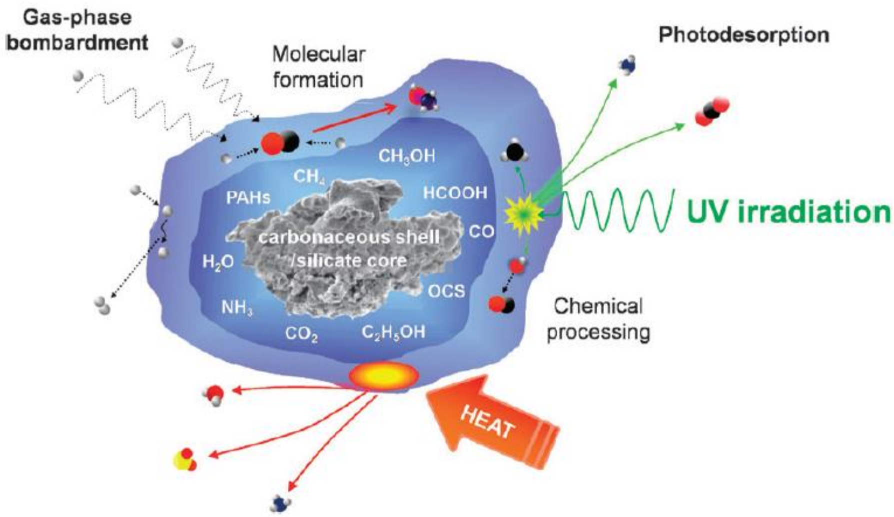

Figure 1: Graine surface chemistry is very important Shaw (2022).

3. Chemical complexification of molecules Molecules consisting on many atoms is possible to synthesize only in solid state, via what is known as radiation chemical polymerization in solid phase, which comes from laboratory experiments. And the successes of experimental physics of molecules under conditions close to the interstellar medium (which is known as laboratory astrophysics) over the past 20-30 years can be briefly summarized as follows Munoz Caro and Escribano (2018). Irradiation by Vacuum Ultraviolet with photons energy in the range 6-13.6 eV (VUV), and Cosmic Ray particles (1 MeV – 1 GeV (CR) induced solid-phase radiation chemical polymerization (polycondensation) from ices (H_2O, CO, CO_2, NH_3, CH_4, CH_3OH (the most abundant ices) and their mixtures. Resulting compounds are aminoacids, heavy hydrocarbons and other organics synthesized at low temperatures down to 5 K. Sources of corpuscular radiation chosen in experiments are protons, electrons and heavy nuclei (α particles etc.) predominantly of MeV energies beaming from various accelerators and sources (e.g. $60^{C}o$ gun). Sources of UV radiation are photons of 10-12 eV by the hydrogen lamp.

Here we mean radiation chemical polycondensation of methane (CH_4) because polycyclic aromatic hydrocarbons (PAH) and aliphatic hydrocarbons (alkanes, alkens, up to 29 carbon atoms in molecule), are synthesized in prebiotic simulation experiments. Radiation chemical yield of alkanes C_nH_{2n+2} (up to 29 C) received from experimental data Yeghikyan et al. (2001), amounts to $G \sim 1$ synth.mol /100 eV and the fraction of new molecules would be $Q \sim G \cdot D$ where the dose $D_{exper.} \sim 6$ eV/molecule (0.3 eV/amu).

It should be noted that threshold doses in the Far UV experiments in the Ames RC, NASA, USA (Dworkin et al. (2004)) where an ice mixture (15 K) was irradiated (H_2O:CH_3OH:NH_3:CO - 100:50:1:1)

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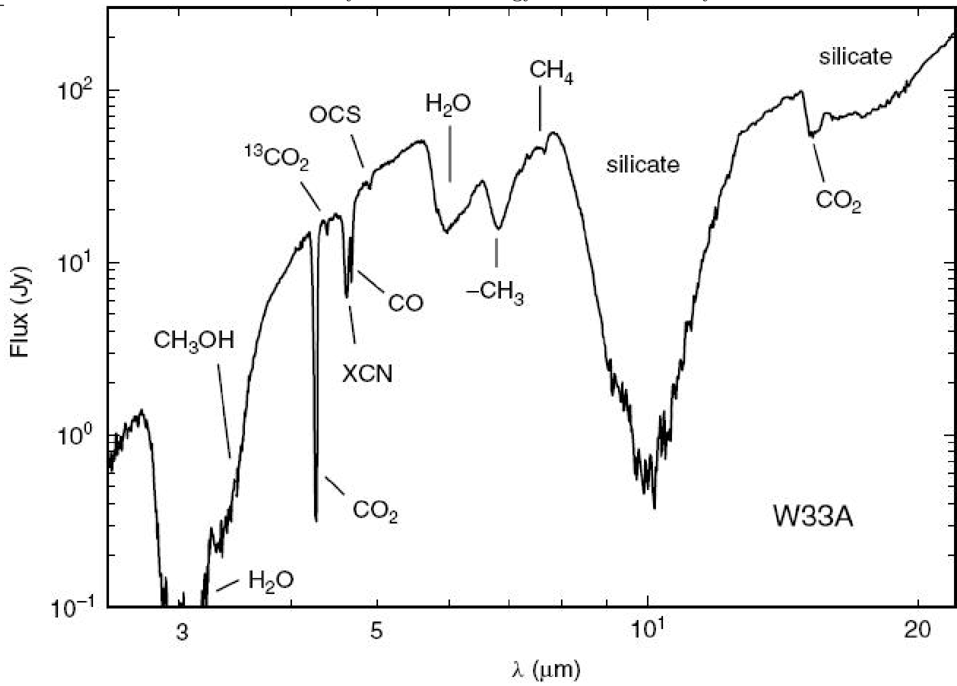

Figure 2: Ices are observed in all star-formation regions.

with photon fluxes $F \sim 3 \cdot 10^4$ photons/cm^2 s, then heavy hydrocarbons and HMT have been originating at doses of $D_{exper.} \sim 25$eV/molecule ~ 1.4 eV/a.m.u. Time-scales are quite appropriate, about Myrs in molecular clouds of SFR (depending on fluxes of radiation and duration of available processing, may be $\sim$ a few million years). Now a few words how to calculate UV photon and MeV particle doses (Yeghikyan (2017)). For UV irradiation

$$\text{n(ice)} \cdot D_i = \int_{\nu_1}^{\nu_2} F_i \cdot \alpha_\nu \cdot d\nu \ \ \text{eV}/(\text{cm}^3 \cdot \text{s}). \tag{3}$$

Here α_ν is an ice absorption koefficient, which is related with cross-section σ_ν via $\alpha_\nu = n(ice) \cdot \sigma_\nu$, cm^{-1}, and $\alpha_\nu(\lambda = 4\pi m_{im}/\lambda$ with m_{im} as an imaginery part of a refraction index. For CR proton flux doses of absorbed energy between E_1 and E_2 would be

$$\text{n(ice)} \cdot D_r = \int_{E_1}^{E_2} F_E \cdot S(E) \cdot dE/M(n) \ \ \text{eV}/(\text{cm}^3 \cdot \text{s}). \tag{4}$$

4. Origin of prebiomolecules (separation from environment by membranes). It should be highlighthed here that Deamer et al. (2002) suggested "membrane first" hypothesis to isolate potential protocell from the enviromnent which needs the lipid bilayer (lipids, pospholipids, et cetera) for aqeous medium to get units of terrestrial life as we know it. This is possible only on the exoplanets surface and chemically active droplets probably could serve as a model for protocells on the early Earth - Zwicker et al. (2017). In general form such idea were proposed by Oparin, 1924 and Haldane, 1955. McCarthy and Calvin (1967) put forwards demands to the potential membrane as polyisoprenoid compounds by their nature McCartly & Calvin (1967). Keheyan et al. (2004), Yeghikyan (2015) enlarged discussion to formulated general conditions for protolife origin.

5. Chiralisation as Homochirality is a key distinguisher of life. Chiral molecules should be important "precursor" to build compounds of first living organisms. Moreover the essense of the Genetic code is based on the Chiralization to accurately self-reproduce what is given. Chiral molecules older than the Earth itself have been spotted in meteors and comets. The most effective mechanism to get enantiomeric enhancement is enantiomerically selective photochemistry, induced by CPL - circularly polarized light of 6 – 13.6 eV - only out of the Earth **?**.

The fact is that the origin of life, as a subject of paleobiology, was studied on the basis of experiments of the Miller-Urey type, when amino acids were found in a mixture of methane, ammonia, hydrogen, carbon monoxide and water vapor under the influence of electrical discharges after some time on the order of a day (sometimes a week) , hydrocarbons, lipids, sugars, etc. were identified. But it should be recognized that these experiments were not adequate, because the amino acids were obtained in the form of a racemic

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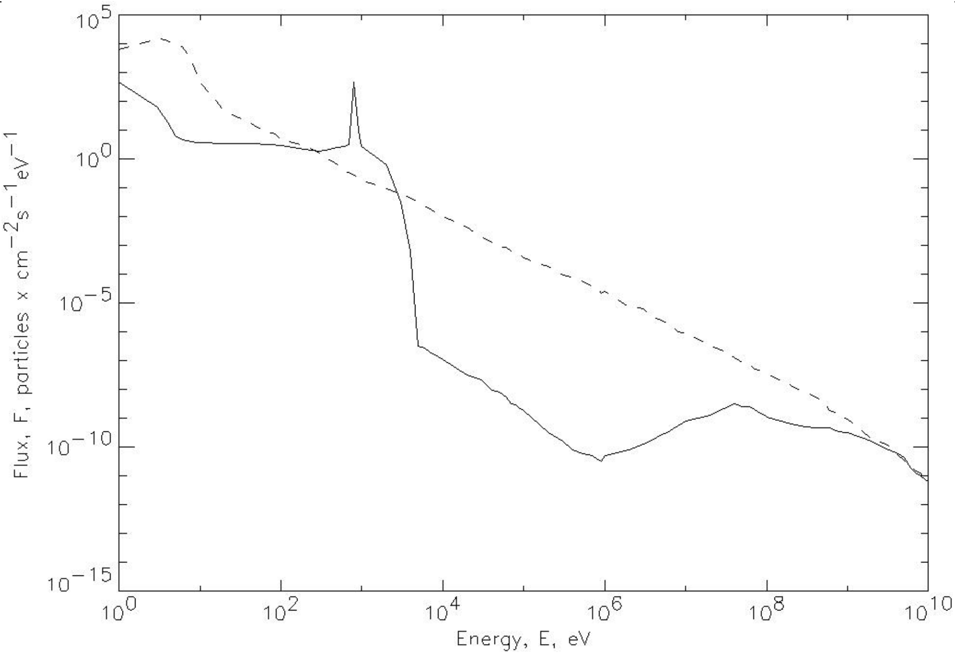

Figure 3: Fluxes of cosmic ray (and solar wind) protons in (solid) and out (dashed) of heliosphere.

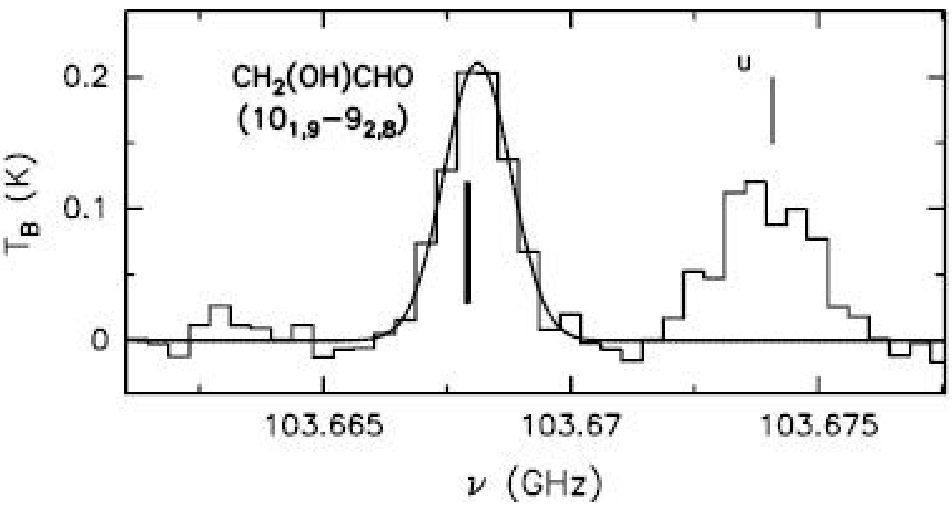

Figure 4: Glycolaldehyde in hot molecular core (HMC, Beltran et al., 2009).

mixture, without a predominance of any (left or right) form, which is important for self-reproduction (and genetic code). For asymmetric synthesis, a carrier of asymmetry is required, in this case photochemical polymerization reactions caused by circularly polarized light in the photon energy range 6-13.6 eV. Other processes that cause molecular symmetry breaking during synthesis are much less efficient (?). In any case, asymmetric synthesis was not possible on Earth; the degree of polarization from scattering of sunlight did not exceed several percent, with the required 20! There are not so many such places with the presence of both the necessary molecules and the radiation demanded; these are either star formation regions of a molecular cloud, next to which a supernova with necessary radiation exploded or disk around a newborn star. Details of transfer such a radiation are still under discussion.

It is also little known where in fact these molecules come from: natal cloud, disk around a star or they may be are synthesized on the exoplanet's surface ?

It turns out that approximately the first half of the age of the Universe, 13.8 billion years, was absolutely unsuitable for the existence of prebiomolecules, such as amino acids and hydrocarbons. They, of course, were synthesized and then destroyed, since the dose of hard radiation exceeded the carbonization threshold, that is, they decayed and simultaneously hydrogen was displaced from mentioned complex compounds, and this process is known as carbonization. Preliminary calculations show (formulae 3-4) that during first 5-7 billion years after the Big Bang the calculated dose in star forming regions was over 1000 eV/amu, which is over the carbonization dose, and only after that this decreased down to 50 eV/amu. Also properties of

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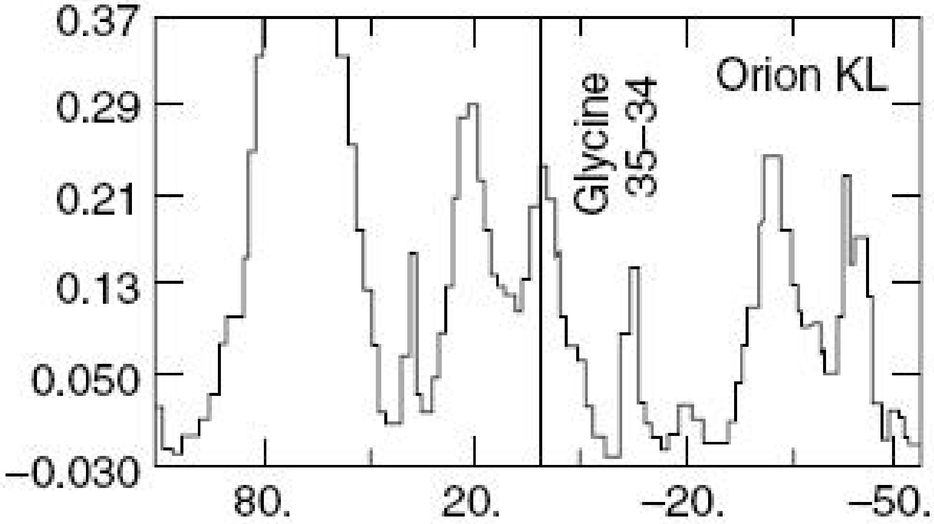

Figure 5: Glycine ($C_2H_5O_2N$, 206.468 MHz), (optically not active), Kuan et al. 2003

Compound class	Concentration (ppm)
Amino acids/CM meteorites	17–60
Amino acids/CI meteorites	~5[a]
Aliphatic hydrocarbons	>35
Aromatic hydrocarbons	3319[b]
Fullerenes	>100[c]
Carboxylic acids	>300
Hydrocarboxylic acids	15
Dicarboxylic acids and Hydroxydicarboxylic acids	14
Purines and Pyrimidines	1.3
Basic N-heterocycles	7
Amines	8
Amides linear	>70
Amides cyclic	>2[d]
Alcohols	11
Aldehydes and Ketones	27
Sulphonic acids	68
Phosphonic acids	2

Figure 6: Carbon containing species in meteorites – amino acids with enanthiomeric excess !

optical activity under irradiation and over-radiation has not been verified yet. So we came to the conclusion that terrestrial form of life based on aminoacids and hydrocarbons probably was the first.

3. Conclusion

1) The biological evolution of prebiomolecules on Earth was preceded by chemical evolution outside the Earth, in star formation regions, and probably in the disks of newborn stars..

2) Calculations show that 13.8-7 billion of years the dose $D > 1000$ eV/amu, which is greater than the laboratory threshold value and should have led to carbonization.

3) Only after that, 7-5 billion of years ago $D < 50$ eV/amu and species needed for the origin of life may exist.

4) Doses were calculated inside of star formation regions.

5) Amino-acids and hydrocarbons begin to exist permanently starting 5-7 billion years ago.

6) Terrestrial form of life was one of the first.

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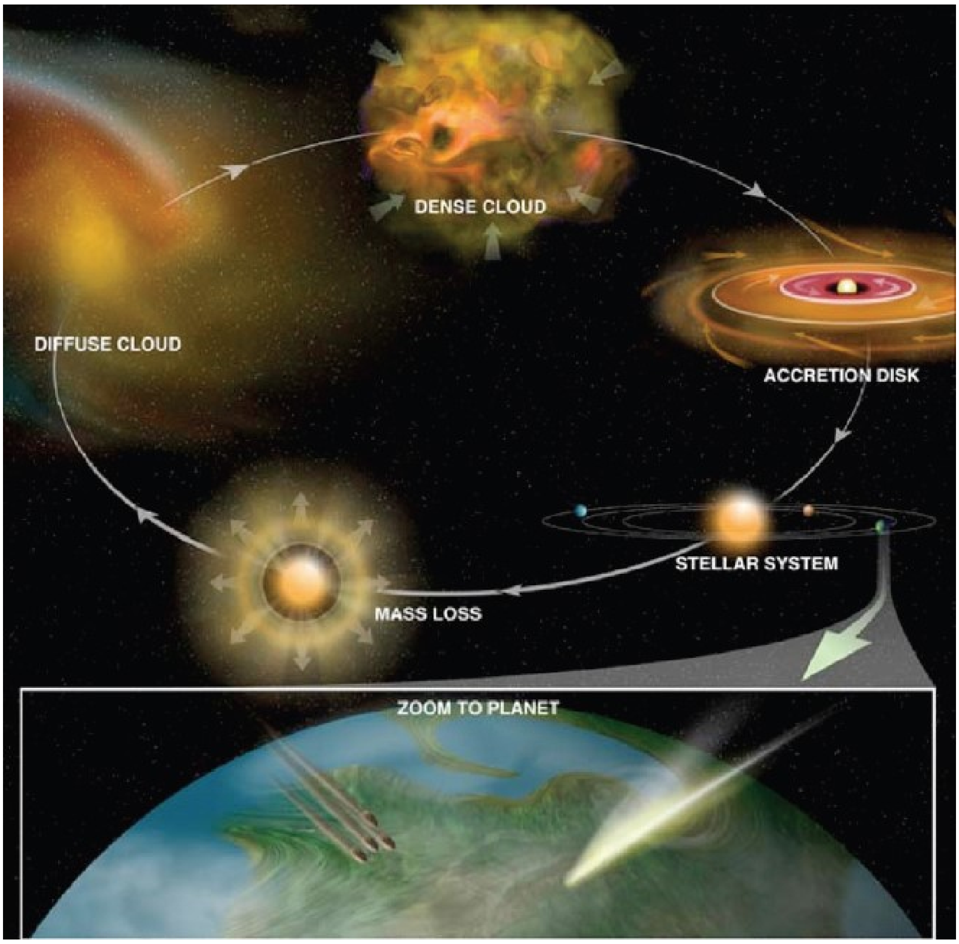
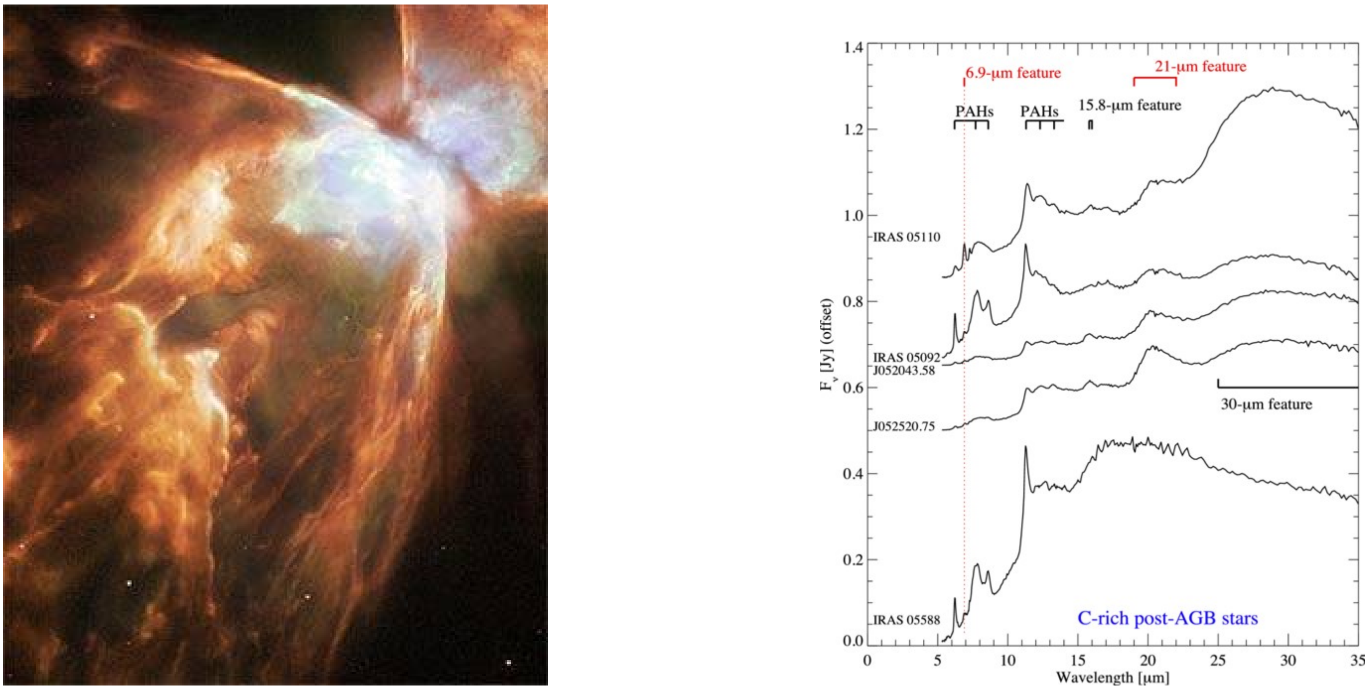


Figure 7: "Organics" recycling in the Galaxy – Kwok, 2010



(a) Cold stellar outflows.

(b) PAH in the post-AGB stars.

Figure 8: Post-AGB stars with spectra where PAH features are visible.

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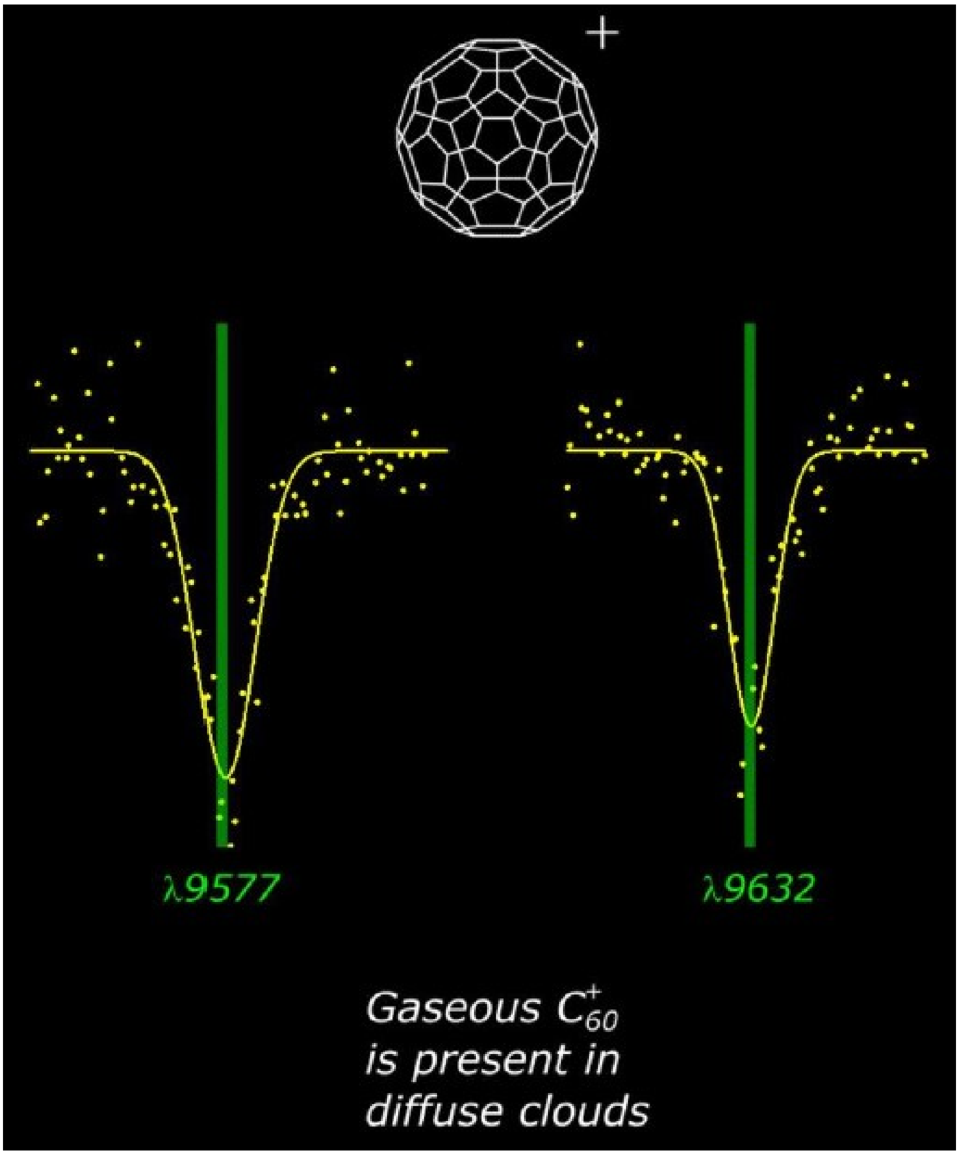

Figure 9: C_{60} in the ISM

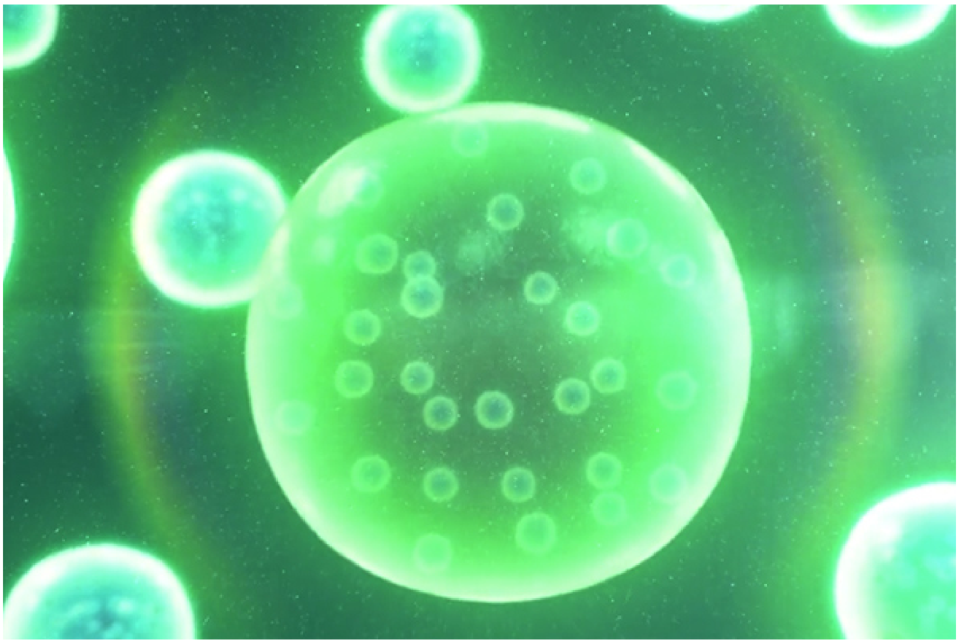

Figure 10: Cell formation - segregation from the environment

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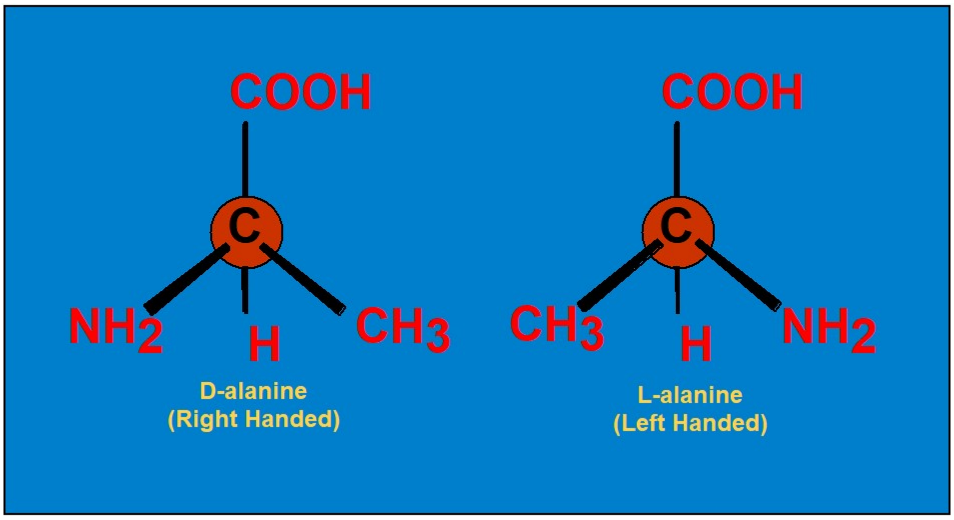

Figure 11: Terrestrial organisms use one enantiomer only

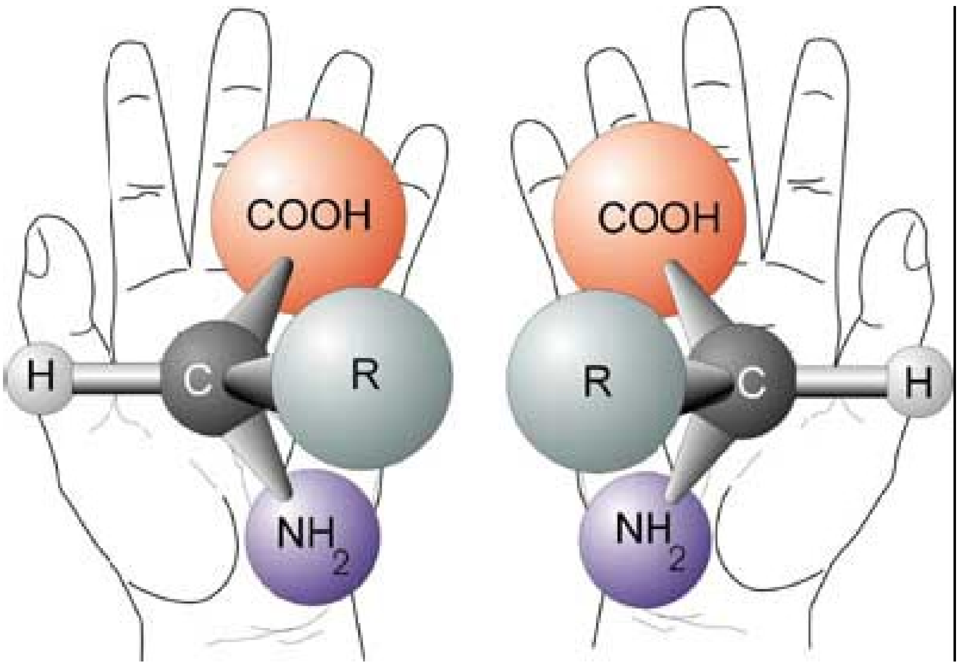

Figure 12: Protein synthesis, gene transcription, metabolism essentially depend on homochirality

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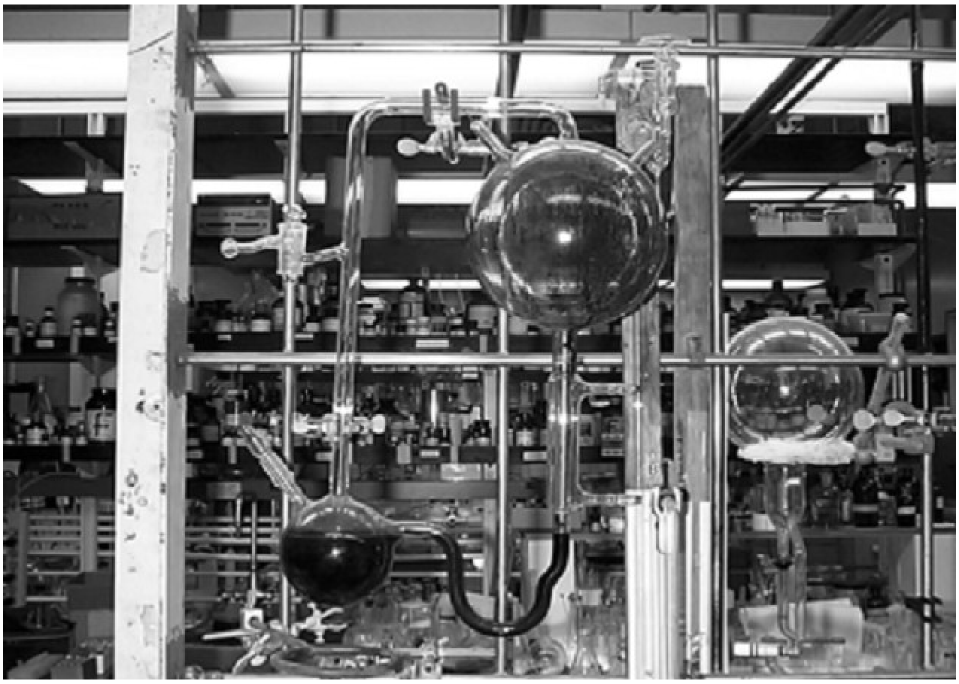

Figure 13: Produced aminoacids are racemic.

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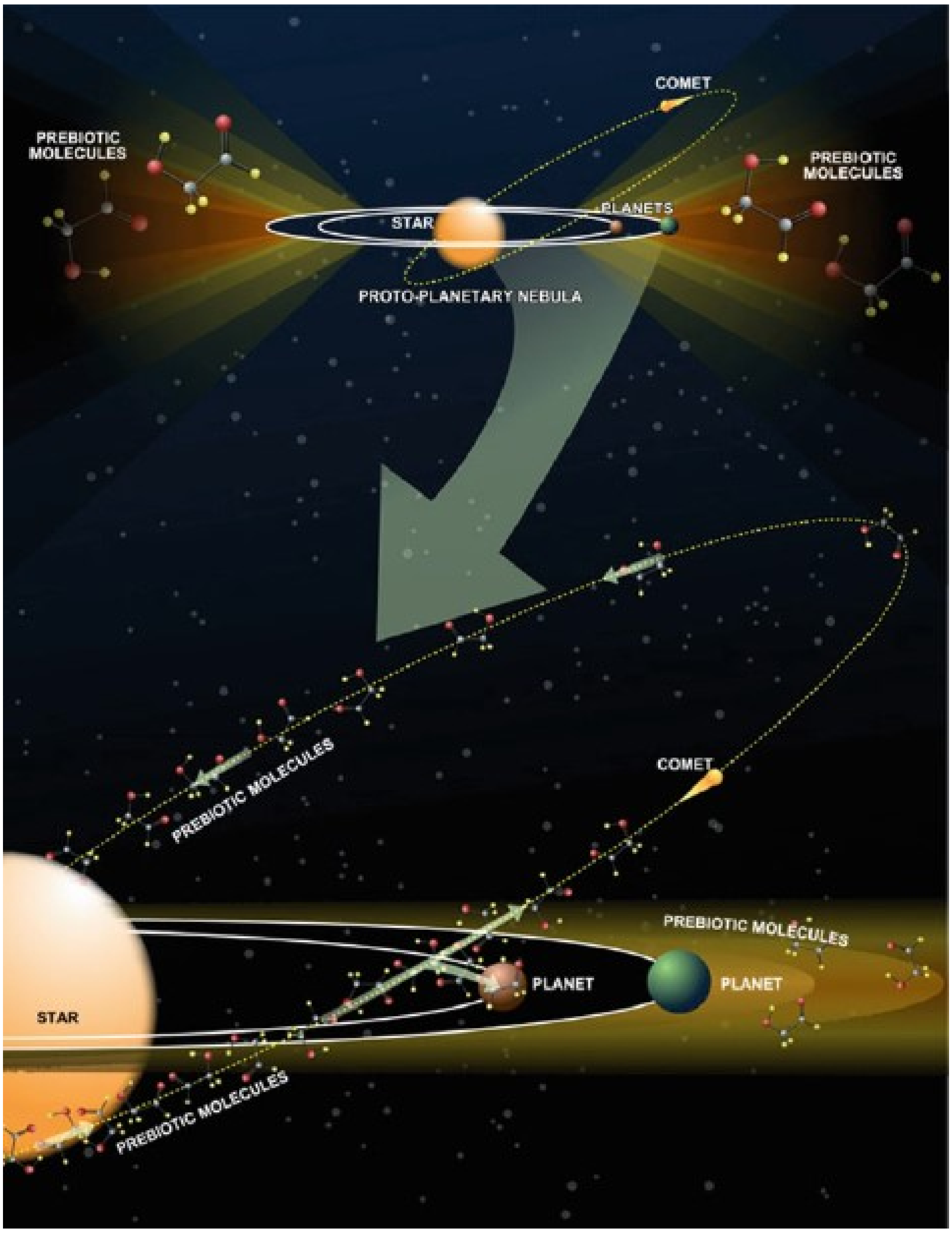

Figure 14: Where do Prebiotic molecules come from ?

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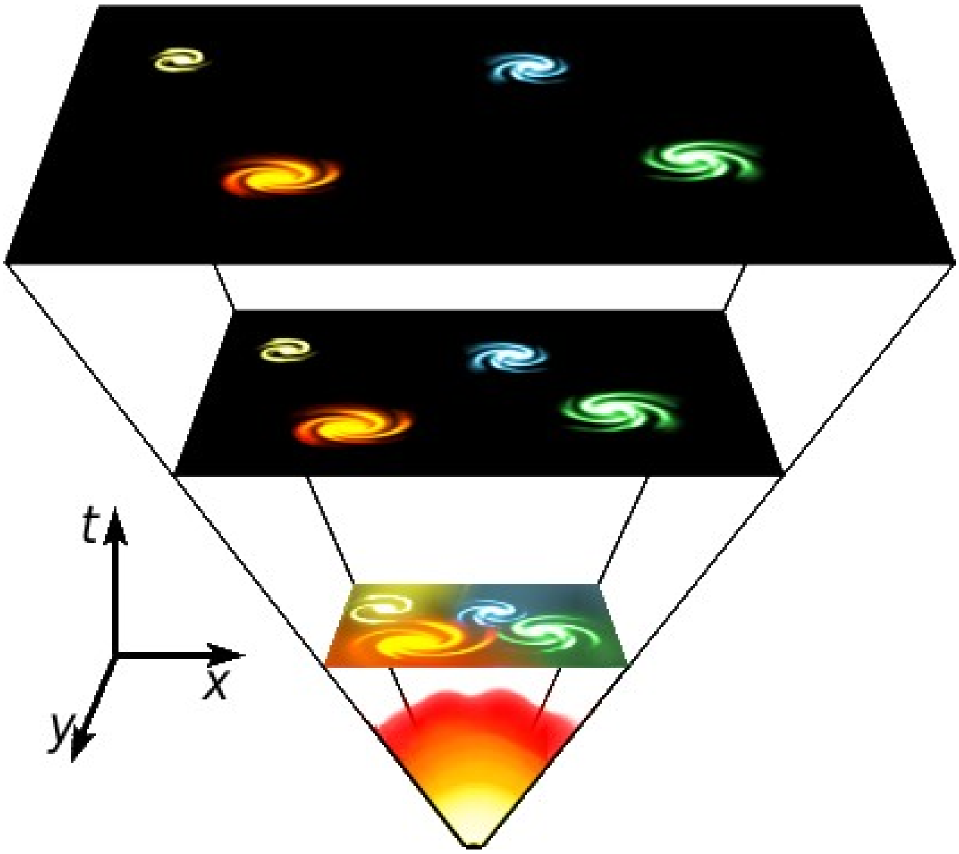

Figure 15: About Possibilities of Life in an Expanding Universe

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