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FROM ASTROCHEMISTRY TO PREBIOTIC CHEMISTRY? AN HYPOTHETICAL APPROACH TOWARD ASTROBIOLOGY

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Abstract. We present in this paper a general perspective about the evolution of molecular complexity, as observed from an astrophysicist point of view and its possible relation to the problem of the origin of life on Earth. Based on the cosmic abundances of the elements and the molecular composition of our life, we propose that life cannot really be based on other elements. We discuss where the necessary molecular complexity is built-up in astrophysical environments, actually within inter/circumstellar solid state materials known as "grains". Considerations based on *non-directed* laboratory experiments, that must be further extended in the prebiotic domain, lead to the hypothesis that if the chemistry at the origin of life may indeed be a rather universal and deterministic phenomenon, once molecular complexity is installed, the chemical evolution that generated the first prebiotic reactions that involve autoreplication must be treated in a systemic approach because of the strong contingency imposed by the complex local environment(s) and associated processes in which these chemical systems have evolved.

Keywords: Astrochemistry, Astrobiology

1 Introduction

Astrobiology encompasses all disciplinary fields, from physics to biology that are of interest to investigate the possibility for life to have emerged on the primitive Earth as well as, possibly, in other environments. However, in this rather precise wording, "astrobiology", linking biology to astrophysics suggests that life has already been observed on other locations than on Earth, which is actually not the case. Thus, this too vague definition does not establish a guideline to link each disciplinary field in order to understand life's emergence processes on Earth. In this short contribution, we propose a hypothesis that retraces organic matter formation and evolution from its appearance in astrophysical environments to its availability in specific ones for the emergence of a prebiotic chemistry. We suggest an approach, involving systemic pluridisciplinarity that may end up in the understanding of prebiotic chemistry, as strongly related to astrochemistry.

We thus propose the following hypotheses: (i) that the biological elements indeed are both present in the gas phase and in "icy" grains in space, semi-volatile molecular species. These conditions are widespread and common in molecular clouds where stellar systems and planets form; (ii) that this situation allows for very complex molecules to form on grains and be preserved for exogenous delivery of organic matter on telluric planets such as on the primitive Earth; (iii) that the solid state chemistry in space is sufficiently complex and intricate that non-directed experiments are warranted and even preferred and (iv) that the composition of the gas and the ices preordains much, if not all, of the chemical composition of life.

2 The molecular evolution of our Galaxy

2.1 The elemental constituents of life

As many stars, the Sun displays in its photosphere, an ensemble of elements, dominated by hydrogen, where the relative abundances are the result of a long suite of nucleosynthesis processes. These processes are obtained

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from the evolution of our Galaxy, through many generations of preceding stars. These “cosmic abundances” are a given characteristic of our “local” interstellar medium where new stars do form even nowadays. These abundances are central to our argument. However, abundances toward a particular line of sight in our galaxy do not reflect nucleosynthesis only. Depletions, elements missing in the gas phase, are commonly observed. Whereas the cosmic abundances are the result of nucleosynthesis, the depletion pattern has nothing to do with it, but translates into the thermodynamical properties of the solids that make interstellar grains. Theories of grain formation based on thermodynamical consideration allow a correct understanding of this well known fact established from diffuse medium interstellar observations. The “average” depletion from the diffuse medium is well known in the astrophysical literature but seems not enough considered in prebiotic chemistry and certainly not in “astrobiology”. A recent re-interpretation of classical data can be found in (Le Sergeant d’Hendecourt 2011). Nucleosynthesis and depletion mechanisms lead to the most abundant elements in the gas phase of the diffuse medium being (H), O, C, N, S and P, those that are available for the starting up of the (organic) chemistry, while the others (Si, Fe. . .), less abundant and buried in refractory grains are lost for any interesting gas chemistry and, more importantly, for solid phase chemical reactions in van der Waals solids, the interstellar ices. Phosphorus, although not much depleted in the interstellar medium is far less abundant. Its presence in outgassing ices from comets in the form of phosphine (PH_3) has been suggested by Boice and Almeida 2012 but not detected up to now (Boice & Almeida 2012). From an astrophysicist’s point of view, if life is considered as merely the outcome of the evolution of the universe, the elemental composition of living systems, as in the case of life on Earth, cannot escape those selected by the physical and chemical laws that apply to these elements. Biomolecules, such as proteins, DNA or RNA, on Earth are indeed essentially based on these 6 major elements H, O, C, N, S and P. Helium although quite abundant does not possess the ability to form molecules and thus can be discarded in prebiotic chemistry. A last and important word of caution though: our hypothesis does not mean at all that life’s evolution does not need all the elements from Mendeleev’s table, but that is obviously a completely different story that cannot be considered in this short paper.

2.2 Cosmic molecular ices and their evolution

In the diffuse ISM, molecules are not present, and the composition of the gas phase as the one of the grains is known from the already described problem of depletion (Greenberg 1974). Entering molecular clouds where the environment becomes relatively protected from UV light because of the refractory dust concentration, molecules can form. As described by many former astronomers such as Oort and van de Hulst (Oort & van de Hulst 1946), elements like oxygen, carbon and nitrogen in a reducing H rich environment will give hydrides, that are H_2O, CH_4, NH_3 prone to form ices in the presence of the cold surfaces of grains. Besides, molecular H_2 must simultaneously form on grains (Knaap et al. 1966). The development of astrochemistry in the field of low temperature gas phase chemistry (ion-molecule chemistry driven by cosmic-ray ionization in the gas) has added to these, essentially CO and its derivatives like HCO, H_2CO (Prasad & Huntress 1980). A major part, actually the quasi totality of the observed molecules in the gas phase, is organic only because the elements H, O, C, N, and S dominate in abundances and availability. The chemistry observed in inter/circumstellar gas cannot be qualified as “complex”: abundances of the detected molecules decrease very rapidly with the number of atoms in the molecule, and the number of different molecules is relatively small (150 about) up to date (ref PCMI website: http://www.pcmi.univ-montp2.fr/). Gas phase reactions in environments such as molecular clouds, are only two-body reactions. They occur in cold media rather unprotected against many destruction routes that preclude the formation of large and really complex species. By opposition, solid surfaces offer locally a huge increase in the molecular density leading to a very high molecular concentration. Van der Waals solids (ices) form the well known and observed “dirty ices” onto the refractory cores. Energetic sources and thermal processes (UV photons and cosmic rays) will allow these ices to evolve toward molecular complexity. Therefore, interstellar grains must be considered as the major chemical reactors of the ISM, which will provide the highest degree of complexity. This solid phase chemistry and its resulting complexity has been apprehended and simulated in the laboratory using non directed experiments on interstellar ice analogs.

Because of the gas species accretion on the grain surfaces, solid state molecules in a given line of sight always dominate in abundances their gas phase counterparts. Energetic processing of laboratory ice analogues from UV photons and cosmic ray particles has led to the detection of some important intermediate molecules through photochemistry processes. This photochemistry leads easily and naturally to the production of organic residues during the warm-up of these photo-processed ice analogues in the laboratory. These residues may then be used as templates for understanding the chemical evolution in the interstellar/circumstellar and cometary media. After reaching 300 K through a slow warming, an organic residue is always left on the sample holder, a semi-refractory material that may cover the surface of most interstellar grains, especially in star forming regions. One of the interesting points about such a simulation is that it constitutes, by definition, a non-directed experiment, largely similar in its methodology to the well known Miller-Urey one. Thereafter, the composition of the produced molecular organic matter is obtained by highly sophisticated techniques issued from analytical chemistry, such as gas chromatography and mass spectrometry (GC-MS) or high resolution mass spectroscopy. In this semi-empirical approach, the evolutionary timescales of the ice can be easily accelerated since a week of experiment roughly corresponds to the lifetime of a molecular cloud. These residues are highly functionalized, and thus remain almost totally soluble in water, an important characteristic for their availability to a possible further prebiotic evolution. Finally, if one admits that the cosmic abundances of the elements are given to forming planets, we propose that the molecular complexity from these organic residues can, and must be considered as a cosmic and universal molecular complexity also given to forming planets. Furthermore, because of the previous discussed elemental depletion, these residues only contain molecules including H, C, O, N, S and P.

3 Organic residues and "prebiotic" materials

Once the planetary system has stabilized, the organic residues formed during the ISM matter cycle, may enter in the composition of various objects, such as comets and asteroids. These interplanetary reservoirs of organic matter (i.e. comets and asteroids), named exogenous reservoir, are thus a source of organic complex molecules containing mainly C, H, N, and O, like amino acids (Sephton 2002), and are considered as one of the main sources of organic matter available from meteorites falls at the surface the Primitive Earth (Pizzarello 2007). Complex organic residues formed in the laboratory have been shown to contain many amino acids when hydrolyzed as reported in (Munoz-Caro et al. 2002; Nuevo et al. 2008; Bernstein et al. 2002). In association with physical and/or chemical energy input, this organic matter can then be used on the planetary surfaces for developing a more complex chemistry, which could lead to the emergence of a prebiotic chemistry. Prebiotic chemistry characterizes the transition between the abiotic chemistry and the biochemistry. It can only occur in a specific environment, in which the development of dynamic networks far from equilibrium driven by a constant flow of matter and energy (Pascal & Boiteau 2011a,b; Pascal et al. 2005) will be favored. Furthermore, because of the complex nature of all the possible interactions involved, these chemical networks display emerging properties. The primitive Earth has been 4.5 Gyrs ago a prebiotic chemical reactor that provided the transition from an abiotic medium to extant biochemical systems. The primitive Earth environment was indeed highly specific, provided by a contingency of astrophysical, planetological, geochemical and chemical events, local conditions and constraints.. An example of experimental research in prebiotic chemistry is the formation and selection of peptides in an environment relevant with the one of the primitive Earth (Commeyras et al. 2004). If organic matter is necessary, as amino acids or derivatives like hydantoin, (de Marcellus et al. 2011) are for peptide formation, it is far from being sufficient. In order to form peptides, an energy input is also necessary through physical sources (e.g. radiation from light) (Commeyras et al. 2004) or chemical sources (e.g. cyanate or carbodiimide) (Danger et al. 2006, 2012). This association of organic matter and of energy sources will drive the evolution of chemical systems that will favor the emergence of peptides. During their elongation, the local environment will provide the selection of peptide chains, the least suited to the environment being recycled through preferential degradation. Therefore we hypothesize that organic refractory residues from ices photochemistry (see (Ciesla & Sandford 2012) for a recent reappraisal of the importance of this phenomenon in the solar nebula), so easily produced in the laboratory may become largely available in comets and asteroids and may be seriously considered as have been taking a major role in prebiotic chemistry toward the emergence of biochemical systems. They could have been delivered onto the Earth, as suggested by the heavy bombardment or the present meteorites (Chyba & Sagan 1992). This exogenous organic residue represents thus an interesting template on the primeval complex chemical input at the surface of any telluric planets.

4 Non directed experiments: a route for "astrobiology" laboratory experiments

Definitely in the laboratory, a complex organic material is produced containing hydrosoluble organic macromolecular fractions. Such experiments may be viewed as a generalization, at the cosmic scale, of Miller's experiment (Miller 1953) that pertained only to the primitive Earth's atmosphere and hydrosphere. Such as the Miller experiment, photochemistry experiments on interstellar ice analogs belong to this class of experiments that may be called non directed ones. What is indeed controlled in these experiments is the natural evolution to which some "trivial" and largely observed interstellar matter (ices) is subjected. Note that the solid state photochemistry of ices cannot be treated in a totally reductionist (mechanistic) way. Starting from a three component ice mixture (actually H_2O, CH_3OH and NH_3), photolyzed by Lyα, it seems difficult, if not impossible to establish the precise mechanistic pathway that will result in the recently measured rather complex composition of the organic residue recently analyzed in (Meinert et al. 2012) that display 20 amino acids and 6 di-amino-acids where its prebiotic significance has been pointed out through the detection of the N-(2-Aminoethyl)glycine molecule, a possible precursor to peptide nucleic acids (PNA). The same remark can be made on the Miller's experiment. As far as the potential "prebioticity" of this material, one must then carefully relates this property to the interaction between the organic matter produced in a plausible astrophysical scenario, taking into account the astrochemistry involved in the presolar and solar nebula, with the environment that will be the one of the primitive Earth, which is the only example we know where life appearance is undeniable. Fortunately, the progressive better knowledge of this primitive Earth (early atmosphere and ocean) will allow investigating the interaction of some organics within a range of parameters (T, pH, illumination...) using the semi-empirical approach of a non-directed experiment. Placed in a prebiotic like-environment, these exogenous materials could take a part in the development of chemical networks as an open input of matter and energetic carriers in a non thermodynamical equilibrium chemical reactor in the laboratory, an experiment to be designed in a near future. This approach will not rely on synthesis chemistry but on a systemic one. Such non directed experiments may help astrochemistry to really enter the field of astrobiology by offering at least a semi-empirical but practical explanation between the molecular universe and the prebiotic one. Furthermore, since astrophysical organic refractory residues can be considered as "universal", exactly in the same astronomical meaning as the one attached to cosmic abundances for the elements in planetary systems, that type of experimentation could also be applied to future exoplanets environments in order to determine if a given exoplanet could reach a stage allowing the development of similar prebiotic chemical networks. Finally we propose a scenario that can be tested from laboratory experiments, unifying astrochemistry, as a consequence of galactic evolution, cosmochemistry in the primitive solar nebula, planetology as the proviso for environments favorable to the emergence of prebiotic chemistry prior to the emergence of life. We consider that, to understand the history of the evolution that precedes the emergence of life, it is important to start the chemical history from stars and molecular clouds where the organic matter, ultimately constituting the feed-up for prebiotic systems, may be born. The track of this evolution provides us with the understanding of the form in which the organic matter could be used for the development of a given prebiotic chemistry in which autocatalytic replication is an essential step toward obtaining a passage from the inanimate to the animate world (Pross 2012). Furthermore, this approach highlights the necessity to understand what sort of environments could be useful for the development of this very specific chemistry. Our hypothesis is not proposed as a firm rule, but as one of the scenarii to be considered, possibly bridging astrochemistry to prebiotic chemistry, and, further, as a guideline to laboratory experiments for astrobiology purpose that may consider this scenario as a systemic process which needs to be treated as such.

5 Conclusions

Astrochemistry is a well recognized discipline. Observations of numerous interstellar molecules, has allowed a better understanding of the physics and the chemistry of the interstellar and circumstellar media. Astrochemistry, especially from an experimental approach, brings us crucial information about the onset and development of molecular complexity, organic in nature, which is a pre-requisite for the starting point of prebiotic chemistry. The accepted evolution of the universe translates to a constant increase with time in complexity of the sub-structures of its components, from galaxies to living cells. Stars provide, through supernovae explosions, an increasing complexity of the interstellar medium with all the elements of the Mendeleev's table that were not synthesized in the early times. Evaporating atmospheres of red giant AGB stars allow for dust nucleation and interstellar grains formation. These grains will then drive the molecular abiotic organic complexity that is for example found on Earth today only in primitive meteorites. It is thus neither surprising nor illogic, to assume that life's emergence on Earth was the result of the natural evolution of the universe, which leads us to consider that the only example known must be the major focus of attention of the astrobiology community. Based on very general astronomical arguments, we point out the fact that the basic elements for life, H, O, C, N, S and P, the ones that are present in proteins and in DNA, with their easiness to form van der Waals hydrides (ices) that can turn into a covalent macromolecular semi refractory solid, cannot seriously be different elsewhere. Moreover, the very special chemical properties of carbon offer an extremely versatile and rich organic chemistry enhanced by liquid water for its role as a solvent and transport. For a chemist, the number of organic molecules is virtually "infinite" a fact that is certainly determinant for prebiotic chemistry and biochemical systems. Thus organic chemistry will provide a real continuum of species which is at the heart of the Darwinian evolution and adaptability of life to ever changing environments. The focus on the studies, intimately connecting astrochemistry and prebiotic chemistry within complex organics, emerging phenomena, and the rise of the very first biomolecular reactions must be viewed as an interdisciplinary and systemic field strongly unified by cosmic evolution. Finally, our conclusions highly recommend that an experimental approach of the development of "minimal life" must be undertaken in a systemic manner that will consider an ensemble of processes in interaction with a given environment. This experimental approach, although interdisciplinary in nature, must also involve a systemic management involving a true interdisciplinary approach of this field where scientists from different disciplines must be able to interact closely and equally with each other. Such a systemic management is certainly the most important condition to successfully obtain a clear understanding of emergent phenomena but, as we must recall, at the expense of an impossible fully reductionist approach.

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