Molecular complexity in astrophysical environments: From astrochemistry to "astrobiology"?

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A prebiotic molecule does not exist per-se, but only in a precise environmental context

Abstract. I present in this paper my own view about the intricate problem between 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 as we know it on Earth. Using arguments from observational astrophysics, I propose that life cannot really be based on other elements that the ones organizing our own so that other life forms based on totally different elemental and molecular processes are highly improbable. As a consequence terrestrial-type environments are probably the most favorable ones to life's "emergence" and subsequent evolution. Discussing molecular (organic) complexity, I show where this molecular complexity is located in astrophysical environments, mostly within inter/circumstellar solid state materials known as "grains" which, at least partly, end up in comets and asteroids and finally on planetary surfaces as meteorites. Considerations based on *non directed* laboratory simulations experiments, recent results regarding chiral asymmetry in potentially prebiotic matter and the possible explanation to the determinism about the choice of the L sign of the enantiomeric excesses in meteoritic amino acids, following a plausible astrophysical scenario, lead to the idea that the origin of life on Earth was indeed the result of a rather deterministic phenomenon, albeit difficult if not impossible to apprehend in its intimate mechanisms via a complete understanding of all the processes involved. Finally, the crucial point in supporting the idea of life's ubiquity and wide distribution in our Galaxy (or universe?) lies in the fact that planetary evolution, another astrophysical argument, is a major and very strong constraint for the development of life above its "minimal definition". Life, particularly the complex and evolved one, could be indeed very rare in our Galaxy, although the very large number of exoplanets may be a counter-argument to this statement. However, the deterministic nature of the processes at the origin of life on Earth, the only example we know, together with the progressively increased knowledge of the early conditions on telluric (exo)-planets and in particular those on our primitive Earth, where life did indeed appear, may render possible, in a near future, a semi-quantitative estimate of its occurrence in our Galaxy as well as major improvements in the field of prebiotic chemistry, possibly linked to the one of astrochemistry.

1. INTRODUCTION

In astrophysical circles, the idea that molecular complexity and the origin of life *as we know it on Earth* are strongly connected through cosmic evolution, dates back, to put it shortly and in modern times, to Stanley Miller's experiment [1] followed by the progressive discovery that complex organic molecules are "ubiquitous" in many and various cosmic environments and on large scales in our Galaxy such as in inter/circumstellar and in the Solar System environments and also, by analogy, within protoplanetary disks where exoplanets do indeed form as recently observed [2]. This statement comes not only from astronomical observations but also from cosmochemical arguments i.e. the analysis of primitive carbonaceous meteorites and micrometeorites as discussed in this book by Rémusat [3] and Engrand [4].

As far as life's ubiquity is concerned, it is sometimes confusing to read, in many scientific publications related to interstellar molecules, that water, H_2O, the most abundant molecule after H_2 in the Galaxy, if discovered in "any" astronomical object, and whatever its physical nature (gas, solid or, rather exceptionally rarely, liquid) is considered as a strong argument in favor of a possible wide distribution of life. If indeed (liquid) water is a prerequisite for life on a planetary surface it is by no means a guarantee of life's presence.

As molecular complexity is concerned, the detection of barely more than 150 (and rather simple) molecules [5] , the vast majority of them organics, in the gas phase of the ISM, sounds already as a direct "proof" for life more than probable extension almost "anywhere". Yet, organic chemists buying their chemicals from the "shelf" are able to see that more than 500.000 organic compounds are for sold in many catalogs from chemical companies. We must keep in mind the fact that most chemists claim that the potential number of organic compounds, natural or man-made, is virtually infinite. Clearly, the "complexity" so much emphasized by astrophysicists has nothing to be compared to the one just hinted by chemists, or even worse, by biochemists and biologists who, above chemical complexity, must also deal with highly complex processes, involving non linear and retroactive ones that are, at the present time, absolutely not understood in a global theory of the origin of life. Nevertheless, the vast majority of astrophysicists assumes that life is a quite common feature of our universe whereas the opposite is discussed by many in the biologists community. To formulate it pedagogically, astrophysicists stick with Miller's results [1] when biologists remain under the influence of Monod [6].

In 1828, the German chemist, Friedrich Woehler, ended up with the "vitalism" theory by abiotically synthesizing urea, a real surprise at that time which was much later, somehow and very generally explained by Erwin Schrödinger in 1944 in his famous book "What is life?" [7]. Indeed, the basic mechanisms governing the "laws" of biology were precisely shown as being just the result, at a reductionist level, of perfectly understandable, if not at that time all fully understood, physical laws. In a profound sense, there are no "laws" in biology that cannot be reduced to the first principles of physical laws, which explains why physics is so much and so soundly considered as the "mother of all sciences" as well as why it is impossible, given the detection of a planet and its location respective to its star to "a priori" assert the presence of life on it.

Following the simultaneous ideas of Alexander Oparin and John Haldane in the first part of the 20th century, and actually deduced from the intuition of Charles Darwin (even though only, in its correspondence following the publication of the *Origin of Species*!), the concept of a sort of primordial soup where all the nutrients and ingredients necessary for life's "emergence" had been present at some early times on the primitive Earth, Stanley Miller [1] did perform, on the precise indications of Harold Urey [8] an experiment in which, simulating early Earth's atmospheric gases composition and physical parameters, in particular free and low entropy energy from ultraviolet (UV) photons from natural shining, the synthesis of many complex organic compounds of assumed (pre)-biological interest, namely amino acids, as well as various carboxylic acids. This impressive result has strongly marked fifty years of research on prebiotic chemistry. However, such experiments have not really ended up with "living organisms" of any sort or at least, even not with what is called, in our modern times, autocatalytic molecules able to replicate themselves not only within the framework of non-directed experiments but even in the context of carefully directed ones. From Miller's primordial soup to the RNA world, the experimental gap remains overwhelming.

Non directed experiments, based on simulations, are applicable to natural evolution of physical and chemical systems in a given environment which determines this evolution, a concept that is often not considered but should be central to this problem given the enormous numbers of apparently free parameters involved in the process of apparition or emergence of life in the seemingly long but finite time of planetary primitive evolution. As a matter of fact, a full reductionist approach to the origin of life is probably impossible especially if one realizes that Miller's experiment, more than half a century later, is still under the prospect of a complete mechanistic explanation even without considering its further application to early Earth's environment and the precise nature of the emergence of living systems.

Such a failure must be recognized in the "astrobiological" community who should consider hopefully more efficient approaches toward the understanding of the general lines of cosmic evolution possibly leading to life's apparition at the surface of a planet in a very most *natural* way as it has been the case around 3.8 Byrs ago or earlier (?) on our planet. As a matter of fact, the loss of the initial conditions on the primitive Earth, the possibility of simultaneous different environments on the surface of the Earth itself has led to a slightly less deterministic approach based on "fuzzy logic" to consider prebiotic chemistry by the group of Reisse [9]. Fuzzy logic and non-directed experiments pertain to the same class of approaches, even if the first one appears more pessimistic than the second.

At the same time than Miller, actually just four weeks before, John Watson and Francis Crick [10] published the discovery of the double helix structure of DNA and formulated very soon the idea that, above simple physical laws, but intertwined with them, the genetic code was the essential and universal basis for life's perpetuation and evolution. The idea that between Miller's experimental result and Watson and Crick's helical structure of DNA, there was just a "small" experimental and reductionist gap has been a widespread illusion during half a century not to mention the fact that if the origin of life is a problem of its own, the origin of the genetic code is an even more challenging and mysterious one. Thus from "astrochemistry", strictly speaking, which is at the heart of this present workshop, to the development of bio-chemical even very simple systems, the gap remains not only huge but overshadowing a problem that is embedded in a sterile fight between reductionism and emergence, neglecting the possible role of non directed experimentation that may help to understand semi-empirically the problem of the origin and early sustaining of self-replicating molecular systems capable of some (Darwinian?) evolution which is the minimal definition of life for a physicist and must be considered here merely as an *operational definition* for further investigations. The first step in the solution (minimal life) is conceptually amenable to test-tube experiments where prebiotic chemistry may be considered as the conjunction between astrochemistry and plausible further evolution at the surface of telluric planets, the Earth in particular, where life indeed appeared being so that our planet must be considered as an object of particular attention. The second, the one of the build-up of the genetic code and the subsequent long lasting Darwinian evolution does not refer, strictly speaking to astrochemistry and is clearly of a different nature.

The goal of this paper is to establish a few facts and principles by which the problem of the origin of life, as we know it on Earth, may be scientifically and on a conceptual basis, considered with some chances of improvement in defining the basic external (in this case astrochemical) and environmental (in this case, planetological) mechanisms by which life may have "emerged", a term generally not accepted by most physicists but which will probably for long remain incontrovertible in this "fuzzy" scientific domain. The important problem of the ubiquity/distribution of evolved life in the universe is however another matter because it seems strongly connected to another astrophysically related discipline, planetology, whose subtle but decisive influence dictates, after the emergence of living systems (or in our case, minimal life), the conditions for their survivability and possible further development and evolution. After all, if a fossil and alien pre-RNA strand is finally found on Mars, nothing will replace the beauty and fun of a nice little white (or pink?) rabbit [11] so common on Earth without even mentioning here the presence of intelligent beings, all these beings, rabbits included, that are indeed the result of ∼3.8 Byrs of painful and intricate Darwinian evolution from the first truly biomolecular reactions.

The next sections will deal with a few astrophysical facts that somehow impose the major ingredients of life not only from an elemental point of view but also, as proposed here, from a molecular one, only based on astrochemistry considerations. These considerations are often underappreciated by the astronomical community which, for historical reasons, still focus onto the gas phase evolution of the interstellar medium which remains a medium of relative molecular simplicity whatever the apparent complexity of the chemical networks are considered nowadays to reproduce the observations [12]. The solution may not come from this branch of astrophysics if only because free flying gas phase molecules, as complex as they can be, will not easily reach undamaged the surface of a telluric planet. Glycine, the

first amino acid, so many times claimed to be detected by radio astronomical methods in the gas phase, does not have here any precise prebiotic significance in this context because the word "prebiotic" will certainly profit of a better and much more strict definition. As largely emphasized by Reisse and his team [9], glycine in itself, does not constitute a prebiotic molecule if discovered in space because the word prebiotic must indeed reflect a prebiotic material specifically at work in a given ecosystem that will allow the "emergence" of life. Finally, the use and abuse of the term "astrobiology" should be criticized: this term is no more than an oxymoron, a double rooted word containing its own contradiction, as recently described by [13]. Astrochemistry may lead to prebiotic materials on suitable planets and in particular on the once primitive Earth, prebiotic chemistry will depend at large on planetary conditions that may be explored as our knowledge of the early Earth (and Mars) improves but, to understand the process at the molecular origins of life requires a real focus on true scientific issues.

2. COSMIC ABUNDANCES, DEPLETIONS AND THE BASIC ELEMENTAL INGREDIENTS FOR LIVING SYSTEMS

Here, I shall briefly discuss one of the central points of living systems, based on what *we know from the only example we have at our disposal: life on Earth*. However, to go further, I show that, given the conditions encountered in the Interstellar Medium (ISM), i.e. the cycling of the solid state material from the nucleation of interstellar grains to their incorporation in planetary forming systems or their destruction in newly forming stars, the elemental composition of any living system is indeed quite restricted no matter the number of elements in the Mendeleev's table. This discussion is centered on *astrophysical and astrochemical* evidence pertaining to the elemental and molecular composition of the interstellar medium (ISM) but also further, imposed on the very first biochemical systems since, as well known, the RNA, DNA and ATP molecules do contain only the following 6 elements: H, O, C, N, S, P.

2.1 The cosmic abundance of elements

Life on Earth is based *exclusively* on 6 major elements H, O, C, N, S and finally P that enters the backbone of DNA, and are present in the ATP molecule. One may wonder if this is an "a priori" general (intrinsic to biology) law or if this occurrence is due mostly to "chance". As an astrophysicist, if life is considered as merely the outcome of the evolution of the universe, I explain below, using simple arguments, why the elemental composition of living systems cannot escape those selected by Nature, the latter meaning simply the ensemble of physical laws which govern the evolution of the universe. As a corollary, I will then propose that life, *as a minimal system*, cannot be related to other elements unless considering entirely new laws and systems, that are, for the moment, outside of the true scientific field.

Earth, as any planet in our Galaxy, is orbiting a star, the Sun, which is, like the Solar System, 4.556 Byrs old. As many stars, the Sun displays in its photosphere, an ensemble of atoms, dominated by hydrogen and helium, where relative abundances of the various elements are the results of a long suite of nucleosynthesis processes obtained from the evolution of our Universe, through many generations of preceding stars, a process which is now really well known and has dominated the history of astrophysics of the middle of the 20th century (see [14] for an excellent textbook on the evolution of the matter in the universe). These relative abundances of elements are called "cosmic abundances" and are a given characteristic of our "local" interstellar medium where new stars do form even nowadays (note that local here implies however extremely vast parts of our own Galaxy and concerns billion of stars). Although cosmic abundances tend to vary somewhat from place to place, following possible local discrepancies in peculiar stars, I shall use, for the purpose of my discussion, classical cosmic abundances, relative to hydrogen, such as the recently compiled ones from a large literature survey, pertaining to cosmic abundances in the Sun's photosphere, the composition of CI chondrites and some discussion about depletions, i.e. the amounts of some missing elements that are presumably locked in interstellar grains [15]. Cosmic abundances for important elements are found below, in Table 1, adapted from [15].

Table 1. Cosmic abundances of major elements (II a and II b stand for major volatile elements involved in life processes (a) and minor ones (b). Abundances relative to H are given in logarithmic scales on the middle column. The right column gives the measured depletion toward one particular cloud (adapted from [15]).

Elements	Symbol	Log Solar Abundances n(H) = 12	ξOph Cloud abundances	Physical nature
Hydrogen	H	12.00	12.00	**Gaseous**
Helium	He	10.99	–	
Carbon	C	8.39	8.14	
Nitrogen	N	7.93	7.90	
Oxygen	O	8.69	8.48	**Volatiles (IIa)**
Sulfur	S	7.33	7.45	
Phosphorus	P	5.45	5.07	
Fluorine	F	4.56	4.26	**Volatiles (IIb)**
Arsenic	As	2.35	2.16	
Magnesium	Mg	7,54	6.33	
Silicon	Si	7.54	6.24	
Iron	Fe	7.45	5.24	
Nickel	Ni	6.25	3.51	**Rock-forming**
Sodium	Na	6.33	5.36	
Calcium	Ca	6.36	2.61	
Titanium	Ti	5.02	1.91	

Abundances toward a particular line of sight allow to calculate the amount of missing elements in the gas phase which are naturally supposed to be locked in grains and thus unavailable in the gas. Note at this point that, if the cosmic abundances of each element (in the Sun's photosphere for instance) is the result of a long nucleosynthesis process and star evolution, the depletion pattern, which is discussed in the next section has nothing to do with nucleosynthesis but somehow translates into the thermodynamical properties of the plausible and observed solids that make interstellar grains.

2.2 The depletion pattern and its significance for life basic elements

"Heavy" elements, actually heavier than He (intermediate elements before C are not considered here), are not synthesized in the Big-Bang but in nucleosynthesis processes in stars and quickly expelled by the explosion of supernovae to enrich the Galaxy in all the known elements. Stars do form continually in our Galaxy, out of a gas that is progressively enriched in these elements. At the end of their lives, stars of intermediate masses (1.1 to 5 solar masses), go through a phase of expansion known as the AGB phase, in which they lose to space their external layers. AGB stars are the real and most probably the dominant factories of dust grains. Although not known in the fullest details, grain formation mechanisms regarding nucleation and condensation reactions are, to the first order, pretty well known and giving a very good idea of the elemental composition of the dust grains that are observed in the diffuse interstellar medium.

As a matter of fact, these theories of grain formation and, in particular, equilibrium condensation theories based on thermodynamical properties of solids, developed in the 70's [16] and variants (see [17], for a recent review) allow to understand, to the first order, a well known fact from diffuse medium interstellar observations, known as the elemental depletion pattern. Although established progressively from increasing data from early ultraviolet satellites measurements in the early 70's, the missing gas phase elements were not attributed to depletions within interstellar grains until 1974 in a visionary paper by J.M. Greenberg [18]. Note in passing that, the observed depletion pattern makes it very clear
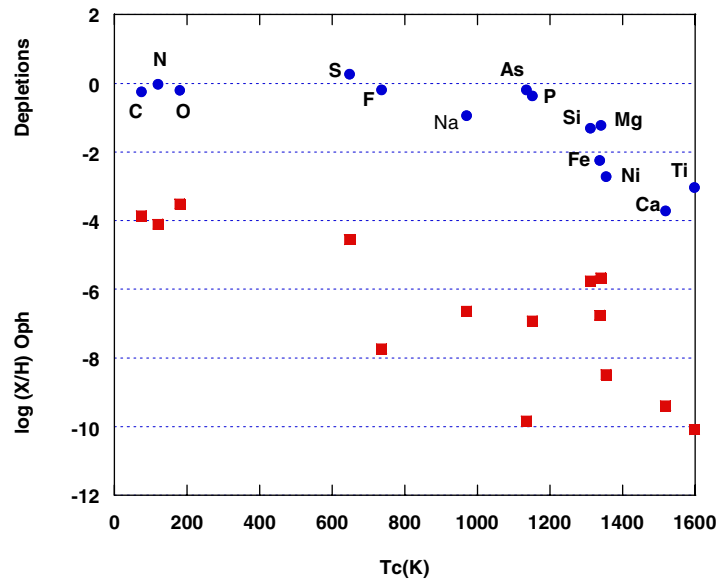
Figure 1. Elemental depletion pattern (blue) and corresponding abundances relative to H (red) in the ξ Oph cloud (adapted from [13]) as a function of condensation temperature. Elements close to the zero depletion line, (H), O, C, N, S , P remain in the gas phase (blue) and are also cosmically abundant in red (although not so much for P and certainly not for As, see text). They are the elements that make RNA and DNA and are thus essential for the basic mechanism of living systems. Depleted elements by more than a dex are lost in the solid phase and moreover naturally under abundant (red) to participate in gas phase chemistry and further molecular complexity.

to know the average grain composition from an *elemental* point of view, although their true chemical (and mineralogical) compositions remain much more elusive and difficult to establish.

The "average" depletion pattern of elements observed from the diffuse medium observations is well known in the astrophysical literature [15] but seems not enough considered in astrochemistry and certainly further, in "astrobiology". I propose in the following to summarize what can be deduced from such a pattern. Let me first consider the most logical and mostly used presentation of the depletion pattern, the one where the depletion of each element is given as a function of their temperature of condensation, usually with no further explanation about the physical meaning of this plot given in Figure 1 (upper dots). If the simplest interpretation of this pattern lies in the "volatile" character of the considered elements, such a plot requires a more attentive explanation.

One must appreciate that this plot is an "educated" choice because it emphasizes the fact that refractory elements are trapped in grains whenever some do remain in the gas phase. However, caution should be taken with such a graph because a given element, C for example, can be found in a very volatile phase, e.g. CO, or in a very refractory one, diamond, graphite or HAC (Hydrogen Amorphous Carbon) with two totally different condensation temperatures incompatible with the pattern displayed on Figure 1. However, the "magic" of this graph is that it conserves correctly a condensation sequence-driven depletion where minerals and oxides are much depleted [19]. The most abundant elements, O and C, show mild but significant depletions (beware of the logarithmic scale!), simply just because their high cosmic abundances prevent them to all react with less abundant ones. N and S show no depletions at all, because N reacts quickly to form N_2 and follows the route of CO. For S, the situation is less clear but the fact is there is no depletion for it in the ISM. A possible solution may be the fate of iron in the condensation sequence which may prevent S to condense as iron sulfur, leaving again only H_2S which escapes the star and returns to atomic sulfur [20]. Remember that these depletions are valid in the *diffuse* medium and that this scheme is oversimplified for pedagogical reasons.

In supergiant AGB stars where grains are observed to condense, less abundant elements such as Si, Mg, Fe, Al . . . do consume all the oxygen they can to form well known minerals that are *refractory* and become thus mostly lost for the gas phase chemistry. To put it simply, much depends on the O/C ratio in the considered envelopes, remembering that on a global cosmic level, oxygen is anyway more abundant than carbon. When O/C is larger than 1 in oxygen rich stars, all the carbon gets in the form of CO, a gaseous molecule that is thermodynamically very stable and forms at high temperature (3000 K). Si, Mg and Fe will rapidly and at high temperatures (around 1000 K) form silicates that are refractory compounds not so easily destroyed and not available for gas phase reactions in the ISM. Through this process, and because O is so much abundant, these elements get fully depleted from the gaseous phase and will remain so *for ever*. Indeed, the main infrared absorption features observed in our Galaxy (to remain in our local universe) are the 9.7 and 18 μm ones related to amorphous silicates materials. These silicates are usually Mg rich (albeit not always) and iron is very probably trapped in them in the form of nanometers sized metallic grains [21] which explains well [22] why IS grains are aligned in cosmic magnetic fields (either the whole galactic field or, in star forming regions, in a local and stronger magnetic field). Such a fact is revealed through the polarization of the 9.7 μm band which clearly shows this alignment. The CO molecules, leaving the envelope, with the gas and grains, will rapidly dissociate to give atomic O and C. The fate of the most abundant atom, oxygen, is to form H_2O which in turn is quickly dissociated in the diffuse ISM to release remaining oxygen atoms (about $2/3^{rd}$ of them).

When O/C is under unity in carbon rich AGB stars (about 20% of the total dust grains production), all the oxygen is then trapped again in CO and other elements just form carbides like SiC, FeC and the remaining carbon, the most abundant atom now, will form PAH's and soot. Eventually, part of the carbon can also form in the ISM, very stable and refractory forms of carbon such hydrogenated amorphous carbon. O, C, N, S and . . . P, at least partly or totally for N and S, remain in the gas phase (2/3 for O, 1/2 for C, almost 1 for N and S) according to depletions of the elements as observed in the gas of the diffuse interstellar medium. Thus, these atoms remain in the gas and are somewhat *forced* to react just by the fact that they are the only ones to remain in the gas. Molecules then formed at the onset of the early stages of molecular cloud formation, happen to be, besides H_2, CO, H_2O, N_2, NH_3, CH_3OH, H_2CO . . . for the simplest ones, found indeed in the gas of molecular clouds but *also* in the solid phase (the so-called interstellar ices), permanently *exchanging* between gas and solid and, thanks to the extraordinary and unique nature of carbon, creating an extremely rich chemistry, essentially of organic nature.

To push the demonstration a bit further, imagine that O and C would be even slightly less abundant than Si, Mg, and Fe. Then all O will be found in minerals, all C in carbides. Water would even not exist, neither in the gas, nor in the solid and, more importantly not in the liquid form. Tetravalent C would simply be useless in the form of carbides and the world would be mineral, with the useful elements, those who are semi-refractory and easily soluble in water, lost in a thermodynamic dwell that indeed a solid is.

Finally, a word of caution on a recent work [23] that has considered the possibility of replacing P by As in some bacteria, even proposing life based on As instead of P on "other worlds". If P and As do show the same lack of depletions in the gas phase, it is certainly not the case if one compares their cosmic abundances (even their abundance in the Earth's crust) which definitely favors P over As to make the phosphate bridges over the arsenate ones in the DNA structure.

Lessons from basic astrophysics and astrochemistry just tell us that life based on other chemical elements is unlikely. A last and important word of caution though: this conclusion 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.

2.3 The solid matter dust cycle in the Galaxy

The ISM is a thorough and well mixed place where abundances are, to the first order, the same "everywhere", at least locally. The Sun's photospheric abundances display simply the cosmic
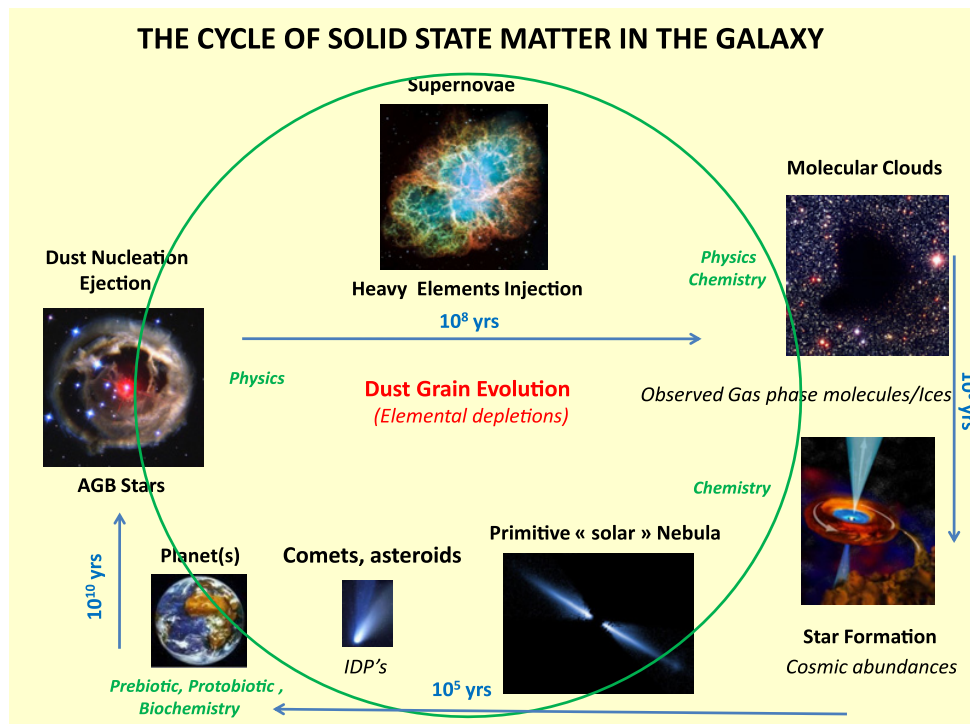
Figure 2. Evolution of (solid-state) matter in our Galaxy. This sketch is self-explanatory and indicative timescales are given on this drawing. Note the very long time span of the Earth's evolution, imposed by the life of its star, the Sun.

abundances from 4.556 GYrs ago, that have not changed by much since then. From the dust formation in the envelopes of late type stars, through its journey in the diffuse ISM, its progressive passage through the molecular cloud phases, it ends-up in the formation of new stars, including planetary systems formation. This scenario proposes a cycle for the life of the interstellar matter, mostly based on the fate of solid matter and strongly connected with the chemistry that may be expected in different environments. This cycle is depicted in Figure 2.

In the diffuse ISM, molecules are not present and the composition of the gas phase as well as the elemental composition of the grains is known from the already described problem of depletion. Entering molecular clouds where the environment becomes relatively, albeit not entirely, protected from UV light because of the refractory dust concentration, molecules can form. As described by many former astronomers, including Oort and van de Hulst [24], elements such as oxygen, carbon and nitrogen in a reducing H rich environment will give, because of the exothermic nature of the reactions (T_{gas} is very low, 10–20 K), *hydrides*, that are H_2O, CH_4, NH_3. Besides, molecular H_2 will be formed on grains since H_2 being an homopolar molecule, a surface is needed to get rid of its formation energy to allow the molecule to stabilize without its atoms bouncing back in the gas [25]. 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 and most of the observed (organic) molecules with the caveat that the observed chemistry is also due to gas/grain interactions through the chemistry of dirty ices that are largely observed in molecular clouds but also, closer to us, in comets. Indeed, as emphasized very early, hydrides are bound to stick onto cold grains and form ices. These ices are just mildly refractory, only held by van der Waals forces (and not covalent ones as in minerals) so that they can condense and evaporate many times.

3. THE ONSET OF ORGANIC COMPLEXITY: THE ROLE OF INTERSTELLAR GRAINS

3.1 Gas phase chemistry

It is not the purpose of this paper to examine and discuss all the aspects involved in the gas phase chemistry that takes place, in the beginning, in what is called "translucent" clouds, where, due to the progressive formation of denser regions, the gas chemistry, mostly driven by ion molecule reactions, starts to form molecules, once H_2 which becomes quickly stable thanks to its self shielding due to its high formation rate, starts being abundant. Indeed, the H_2 molecule is of primary importance for gas phase chemistry since ion-molecule reactions require the presence of H_3^+ from cosmic ray ionization of H_2. Thereafter, the CO molecule is quite abundant, again taking advantage of the fact that O and C are *naturally* abundant in the ISM, as already described. Note that CO will also become quickly self shielded in molecular clouds. H_2O is naturally made, mostly, but not entirely by reactions on grain surfaces. There again, H_2O is abundant because oxygen is the dominant element in the gas phase. Overall, the chemistry of the not too dense molecular clouds cannot be qualified as complex if one pays attention to the detected molecules whose abundances decrease very quickly with the number of atoms (roughly a decade per added atom in a molecule) and to the relatively small number (150 about) of detected species. The list of detected molecules is given in Table 2, a list changing every year by a few units, thanks to the improvements of new instrumentation but at a pace which will marginally allow to consider these gas phase molecules to be important in the formation of large macromolecular entities that are needed for the complex chemistry at the onset of life. Above all, one must not ignore the fact that, on this Table 2, increasing the number of atoms of one unit, roughly decreases the absolute abundance of the compound, relative to hydrogen by one dex, with the notable exception of solid state molecules which remain, in regions of observation (collapsing molecular clouds) two to three orders of magnitude larger in abundance than their gas phase counterparts.

Although gas phase networks built-up to understand the gas phase species and relative abundances may be quite complex and involved, taking into account as many reaction rates and reaction channels as possible (see for instance the large work undertaken within the KIDA database [26]), one must note that gas phase reactions are only two-body reactions that are measurable or that can be calculated or guessed with some good precision. Moreover, one of the characteristic of gas phase chemistry is that it evolves in rather low density media, unprotected against many destruction routes (UV photons, cosmic-rays, dissociative recombination with ions . . .), all events that will preclude the formation of large and very complex species too often abusively called "biomolecules" such as amino acids, for which the simplest one glycine still awaits detection. Besides, the most complex molecules detected nowadays such as aminoacetonitrile observed in Sgr B2 [27], a precursor of glycine, cannot be accounted for by any gas phase reactions network but supposes that the molecule has evaporated from grain surfaces. A route for aminoacetonitrile formation has recently been proposed using icy grains bulk reactions driven by UV photon photochemistry [28, 29]. This last example may not necessarily be seen as the only pathway mechanism for this molecule but it just illustrates one of the capabilities of the presence of grain surfaces to obtain very different and much more complex molecules. Indeed, by opposition to the gas, surfaces offer locally, at a microscopic level, very high densities because they are solids so that they allow the addition of many reactants. They offer also a means to get rid of the energy of formation for exothermic reactions and shielding from UV and cosmic rays when the molecules become progressively encaged in the ices that continuously form on them and protect more complex species. Finally, energetic sources (UV photons and cosmic rays) will allow these ices to evolve toward molecular complexity, a way that has been apprehended and simulated in the laboratory since the mid 80's [30], there again, for astrophysical purpose and more particularly for the subject developed in this paper, using non directed (simulation) experiments on interstellar ice analogs that will be briefly now discussed.

A final comment about Table 2 must be made here. The large predominance of organic molecules observed in the ISM is no wonder, if one simply refers again to cosmic abundances and the observed depletions of the elemental composition in the gas. As a matter of fact, molecules containing mineral

Table 2. List of observed interstellar molecules. Although identified gas phase molecules dominate this list, some molecules are also observed in the solid state under the form of ices. PAHs and recently detected fullerenes are not mentioned in this list.

2 atoms	3 atoms	4 atoms	5 atoms	6 atoms	7 atoms	8 atoms	9 atoms	10 to 13 atoms
H_2	H_2O	NH_3	CH_4	CH_3OH	CH_2CHOH	H_2C_6	$(CH_3)_2O$	$(CH_3)_2CO$
CO	H_2S	H_2CO	SiH_4	CH_3SH	$c\text{-}C_2H_4O$	$HCOOCH_3$	CH_3CH_2CN	$HOCH_2CH_2OH$
CSi	HCN	H_2CS	CH_2NH	C_2H_4	$HCOCH_3$	CH_2OHCHO	CH_3CH_2OH	CH_3CH_2CHO
CP	HNC	C_2H_2	NH_2CN	H_2C_4	CH_3CCH	CH_3C_3N	CH_3C_4H	CH_3C_5N
CS	CO_2	HNCO	CH_2CO	CH_3CN	CH_3NH_2	CH_3COOH	HC_7N	HC_9N
NO	SO_2	HNCS	HCOOH	CH_3NC	CH_2CHCN	CH_2CHCHO	C_8H	CH_3C_6H
NS	MgCN	H_3O^+	HC_3N	NH_2CHO	HC_5N	CH_2CCHCN	C_8H^-	C_2H_2OCHO
SO	MgNC	SiC_3	HC_2NC	HC_2CHO	C_6H	C_7H	CH_3CONH_2	C_6H_6
HCl	NaCN	C_3S	$c\text{-}C_3H_2$	HC_3NH^+	C_6H^-	CH_2CH_2CN	CH_3CONH_3	C_3H_7CN
NaCl	N_2O	H_2CN	$l\text{-}C_3H_2$	HC_4N				$HC_{11}N$
KCl	NH_2	$c\text{-}C_3H$	CH_2CN	C_5N				
AlCl	OCS	$l\text{-}C_3H$	H_2COH^+	C_5H				
AlF	CH_2	HCCN	C_4Si	H_2C_4				
PN	HCO	CH_3	C_5	C_5N^-				
SiN	C_3	C_2CN	HNC_3	$c\text{-}H_2C_3O$				
SiO	C_2H	C_3O	C_4H					
SiS	C_2O	$HCNH^+$	C_4H^-					
NH	C_2S	$HOCO^+$	CNCHO					
OH	AlNC	C_3N^-						
C_2	HNO	HCNO						
CN	SiCN	HSCN						
HF	N_2H^+							
FeO	SiNC							
LiH	$c\text{-}SiC_2$							
CH^+	HCO^+							
CO^+	HOC^+							
SO^+	HCS^+							
SH	H_3^+							
O_2	OCN^-							
N_2	HCP							
CF^+	CCP							
PO								
AlO								

bearing elements such as Al, Si and Fe are known to be essentially circumstellar molecules, just before the onset of solid grains formation. Note that these elements have already disappeared (with one exception, SiNC) from the molecular gas as seen in the second column of Table 2 listing the molecules composed of only 3 atoms.

3.2 Interstellar ices and their energetic by-products in the laboratory

3.2.1 Interstellar ices

Interstellar ices are well known since a very long time, thanks to the advent of infrared spectroscopy in astronomy in the mid 70's. However, it was not until 1979 that water ice was shown to indeed explain
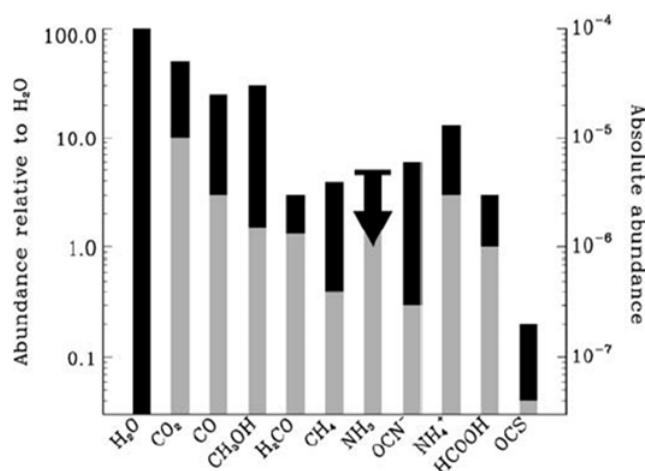
Figure 3. Abundances of observed interstellar ices relative to H_2O. The black extension does indicate variations of these relative abundances from source to source (from [36]). Note that the upper limit on NH_3 (arrow) is now the observed value.

the strong and very broad absorption band observed in the BN-KL object in Orion [31]. A precise identification of this band relies on dedicated laboratory experiments where it could be shown that the IR spectrum of the OH band from *amorphous* H_2O ice did match closely the observed astronomical band [32]. The development of simultaneous astronomical observations in the IR region, in particular from airborne telescopes such as the KAO [33] and larger ground based ones together with the extensive use of laboratory simulations led quickly to the discovery of the solid CO molecule [34], whose observation could also be interpreted in terms of grain temperatures [35], based on the thermodynamic properties of these ices. Finally, the growth of infrared astronomy with IRAS, ISO and Spitzer satellites did allow the detection of many *and* abundant species in the solid phase, under the generic name "interstellar ices", mostly in protostellar objects where ices are detected in the collapsing molecular cloud material that is located in front of the IR source formed by the interaction of the protostar with the infalling material. A list of interstellar ice molecules with their abundances, respective to the water molecule (100) is given in Figure 3. Note that, because of grain accretion of the gas phase species, solid state molecules (H_2O, CO, H_2CO, CH_3OH), in a given line of sight, always dominate in abundances their gas phase counterparts by one to three orders of magnitude. An excellent review on icy molecules can be found in [36] from which Figure 3 is extracted, and complementary information can be obtained in [37].

Before to conclude this short introduction on ices, let me recall that only dedicated and careful laboratory experiments able to replicate the observed spectra have allowed demonstrating the intricate nature of these ices. For example, the formation of molecular complexes (e.g. CO_2:CH_3OH) or hydrates such as ammonia hydrates [38, 39] has been established and explained in the laboratory and the corresponding features (band shapes in particular) in astronomical spectra have been duly observed. Thus, and most importantly for the irradiation experiments described in the following sections, the nature of the *starting* mixtures of the used laboratory analogs are well enough known that simulation experiments can be used as *templates* to explain the growing nature of complexity in the organic material on the surface of interstellar grains.

3.2.2 Astronomical evidence for energetic and thermal processing of ices

Although always debated in the literature, energetic processing of interstellar ices from UV photons and cosmic ray particles has been investigated as early as in the mid 80's. Truly speaking, few direct evidences do exist from the detection of some important intermediate molecules. One of the problems

encountered by IR spectroscopy is its absence of sensitivity relative to radio-astronomy, in particular because, in the solid state, many lines are blended or hidden by molecular interactions between a given molecule and the dominant and very polar species, H_2O. Thus it is practically impossible to record molecules that are present under the level of a few percent that of H_2O. Nevertheless, in 1989, the discovery of the solid state CO_2 molecule, a direct by-product of the UV photochemistry of ice mixtures involving water and carbon monoxide was obtained using the LRS (Low Resolution Spectrometer) instrument onboard IRAS [40]. Remarkably, this discovery was made possible because of model predictions from 1985 [41] examining gas/grain interactions in dense clouds as well as laboratory simulations specially developed to study the effect of UV photochemistry on interstellar ices [42]. The fact that the presence of interstellar CO_2, totally absent and unexpected in the models of gas phase chemistry, because its main formation mechanism is endothermic, was indeed predicted from laboratory experiments, has been largely ignored until its "rediscovery" in 1996 by the ISO-SWS instrument onboard ISO [43]. Other solid phase molecules can also be attributed to energetic processing, where UV photons have usually been more employed than cosmic rays, although it should be stressed that the effects of cosmic rays are remarkably similar, as far as the build-up of more complex species is considered (see for example [44]).

Actually observation of such processes is difficult because of intrinsic properties of water ice making it difficult to observe small abundances species but also because, in a molecular cloud, cold ices in the same line of sight, do mask very efficiently warmer regions where ice sublimates and where, as a result of slow warming up of the grains, for example in hot molecular cores [45], it is nearly impossible to observe the organic material that may remain, as in the laboratory experiments, at the surface on the grains, where all the organic complexity may be found. A counterexample of this situation lies in the detection of the ammonium cyanate bands ($NH_4^+OCN^-$), easily observed in the laboratory and found *in the 3 micron* region in only one object, MonR2-IRS9 where the water ice exhibits a crystalline feature and is clearly evaporating [46].

Other attempts have been performed to detect the effect of UV photolysis with some tentative successes such as in NGC7538-IRS9 where the 5 to 8 micron region may be interpreted by the presence of semi complex molecules such as urea, formamide and glycerol [47]. Although the evidence is scarce, from many bias in the observations, the good knowledge of the molecular composition of interstellar ices and the presence of energetic processing allow experimentalists to use ice evolution, from photo and thermo chemistry, in the laboratory as templates for what may be possible in the interstellar medium, with further evidence for a very complex organic chemistry whose nature is described in the next section.

3.2.3 *From ices to organic residues*

Laboratory experiments on interstellar ice analogs are based on a rather simple experimental concept, matrix isolation spectroscopy [48]. A gas mixture is prepared in a metallic high vacuum line where gas phase molecules mimicking those observed towards protostars (e.g. H_2O, CH_3OH, NH_3, CO_2, CO . . .) are mixed. This mixture is then deposited onto a glass window cooled to the desired temperature (10–80 K). A microwave discharge lamp produces an intense UV photon flux, with a given spectrum [49], mostly Lyα (but not only). These experiments are largely described in [50–52] and we shall not come back on the details of those. Usually, to obtain a thorough photolysis of the bulk of the ice, the mixture is deposited together with the photon flux (simultaneous irradiation) so that the building sample does not appear to be thick in the UV. Thus it is possible, in principle, to adjust the ratio of the number of UV photons to the number of deposited molecules. For most experiments this number is adjusted to one but may actually vary from 0.1 to about 10. One of the interesting points about such a simulation is that this constitutes, in its definition, a non directed experiment, similar to the one of Miller [1]. The knowledge of the ice composition, the environment in which these ices evolve, the subsequent heating when closing a star, for example, in hot core regions where molecules are observed to evaporate from grains, all these processes can be empirically reproduced in the laboratory so that the evolution of the molecular
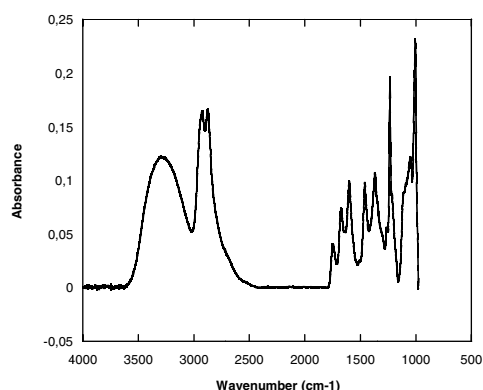
Figure 4. Infrared spectrum of a typical organic residue obtained from interstellar ice analog photochemistry, after evaporation, at room temperature (from [53]).

matter can then be followed by sophisticated analytical techniques such as gas chromatography and mass spectrometry (GC-MS) and many other methods that will be used to analyze the organic residues that are formed during these processes. Note that, in the empirical approach, the evolutionary time of the ice can be easily accelerated since a one week experiment corresponds roughly to the lifetime of a molecular cloud where the interstellar ices do evolve. At the end of the experiment, thus at 300 K, an organic residue is always left on the sample, a semi-refractory material that may cover the surface of most interstellar grains, especially in star forming regions. For the sake of simplicity, we present, in Figure 4 a typical in-situ IR spectrum of such a residue coming from the UV photolysis of an ice mixture composed of H_2O, CH_3OH and NH_3 in a ratio around 2/1/1. Note that these experiments, duplicating the recent ones from [53] are made at a temperature of 80 K to further speed up the reactions in the samples. The ice composition used in the laboratory experiments is close to their compositions in high mass stars molecular regions although CO and CO_2, easily made during photolysis, are not included in this mixture. Many other similar experiments have been performed on these ice photolysis simulations.

The characteristic features of these semi-organic residues can be seen from their infrared spectra which are rather insensitive to the precise ice composition (given the fact that the used mixtures are generally similar) as well as to the temperature of deposition (from 10 to 80 K). An interpretation of the residue spectrum is given in Table 3 where only chemical functions can be identified, besides the HMT molecule already mentioned in 1995 [55].

Actually, many other studies pertain to this organic residue. Among them [56] is one of the most extended and pertinent. The IR spectrum displayed here is very generic and does not change much when similar, but somewhat different relative compositions are considered. These semi-refractory residues are highly functionalized and thus remain almost totally soluble in water, an important characteristic for their availability to a possible further prebiotic evolution if arriving in an ocean on a telluric planet.

3.2.4 Relevance of organic residues to the problem of prebiotic materials

Before I describe the possible relationship between these organic residues and organic matter found in meteorites, it is important to emphasize that acid hydrolysis treatment of such residues, a classical treatment employed to break up the original macromolecules present in them, has held as many as 16 amino-acids [57, 58] as well as carboxylic acids and di-peptides [59]. Although the method is somewhat criticized by its unrealistic parameters (100 °C in 6 M HCl), it can be argued that this procedure just speeds up the hydrolysis mechanism that will take much more time in a primitive but warm ocean.

Table 3. Infrared bands of the organic residue with their chemical identification.

Position (cm^{-1})	Position (μm)	Carrier (mode)
3600 - 3000	2.78 - 3.33	alcohols, carboxylic acids (O-H stretching) and amines (N-H stretching)
2957 - 2945	3.38 - 3.40	carbon chains (CH_3 stretching)
2926 - 2923	3.42	HMT ($2\nu_{19}, \nu_2 + \nu_{19}$) and aliphatic chiains (asym. CH_2 stretching)
2875 - 2872	3.48	HMT (CH_2 stretching ν_{18}), NH_4^+ ($2\nu_4$) and aliphatic chiains (sym. CH_2 stretching)
2150*	4.65	nitriles (C=N stretching)?
1750 - 1745	5.71 - 5.73	esters (C=O stretching)
1675 - 1665	5.97 - 6.00	amides (C=O stretching)
1603 - 1599	6.24 - 6.25	amides NH_2 including POM
1461 - 1458	6.84 - 6.86	NH_4^+ (ν_4) and methyl and methylene groups (C-H bending)
1370	7.3	HMT (C-H scissoring)
1235 - 1233	8.1	HMT (C-N stretching ν_{21})
1006	9.94	HMT (C-N stretching ν_{22})

However, in that case, time is indeed not such an issue since millions of years will be available for this hydrolysis in a primitive ocean and further possible chemistry which may then be really called *prebiotic*.

In the frame of the cosmic evolution of solid materials depicted in Figure 2, collapsing molecular cloud materials will, at least partially, end up in planetary disks and may be integrated as asteroids or comets. CI meteorites such as Orgueil do contain appreciable amounts of carbon (up to 4% r.w.t.). Among this fraction, about a fourth is in the form of a soluble organic material whose molecular composition has been previously studied [60] as elsewhere described in this book [3, 4]. To which extent is there a link between this soluble organic matter (SOM) in meteorites and the organic residue is not yet precisely known but is the subject to intensive studies. Formerly suspected to be the result of contamination and Earth's weathering, new and more sensitive analytical techniques may help to resolve this issue. As well known, even primitive meteorites have known an episode of thermal and aqueous metamorphism so that a study of its effect on original and genuine organics obtained from photochemical reactions as described above may also be considered and can be easily simulated in non directed experiments similar to the ones related to extraterrestrial ices evolution.

Recently, it has been reported that irradiation of ice analogs using Circularly Polarized UV light on the DESIRS beamline on the synchrotron radiation facility SOLEIL in France, has produced a proteic amino acid, alanine, with a slight but significant enantiomeric excess, similar to the ones observed in some primitive chondrites from the solar nebula [54]. In the framework of a plausible astrophysical scenario (see details in [61]), it is then proposed that a direct link between organic materials from primitive chondrites with photochemistry of interstellar ices exists, including a possible photochemistry step using some CPL whose existence in regions of high mass star formation regions is now documented [62]. One argument from this observation is the fact that CPL light of the *same* helicity (L or R) is indeed present over large spatial areas in such regions, areas that are much larger, by roughly a factor 100, than the size of a "solar" nebula. Such an encouraging result relies also on the fact that the experiments using CPL light have used exactly the same parameters than the more classical photochemical ones using non polarized UV light. Thus, not only a prebiotic material may be produced in this way, but it may also contain the chiral asymmetry that is important later from the starting of biochemical reactions [63].

4. NON DIRECTED EXPERIMENTS: A PASSAGE FROM ASTROCHEMISTRY TO "ASTROBIOLOGY"?

Astrochemistry experiments, particularly those related to the study of the evolution of ices, following energetic processes have originally been undertaken to interpret astronomical spectra, especially, 20 years ago, those expected from the ISO satellite whose spectral capabilities opened a new window of observations for the chemistry of molecular clouds [64]. This approach has been altogether very successful to understand the global ice composition as well as the importance of their evolution upon irradiation with UV photons and cosmic rays of energies around the MeV. Definitely in the laboratory, a complex organic material is produced, containing hydrosoluble macromolecular fractions. Such experiments may be viewed as a generalization, at the cosmic scale, of Miller's experiment [1] that pertained only to the primitive Earth's atmosphere. However, the possible dominance of an oxidizing atmosphere (rich in CO_2) is a serious challenge for Miller's hypothesis, even though his experiment remains a chemically pioneering one. This problem may be overcome by the late bombardment of the Earth by a reduced form of carbon that may be found in meteorites or better micrometeorites [3, 4]. Such as Miller's experiment, photochemistry experiments on interstellar ice analogs belong to this class of experiments that may be called non directed ones. Indeed, what is controlled in these experiments is the natural evolution to which some "trivial" and largely observed interstellar matter (ices) is subjected. For example, photon fluxes used in the laboratory allow increasing the kinetics of the reactions so as to obtain in a few days an evolved material that may be very similar to the one that entered the solar nebula after $10^{5/6}$ years of evolution. Note that, on the contrary to gas phase networks and reaction rates which are used to study gas phase chemistry in molecular clouds, solid state photochemistry of ices cannot be treated in a totally mechanistic way. Almost 60 years after Miller's work, the full complexity of the byproducts of his rather *simple* experiment has still not been fully elucidated. The same will be true for the organic residues. Many analytical tools pertaining to physical chemistry will be needed to at most understand the outcome of the experiments and the precise nature of the complex organics formed. A complete reductionist approach of the entire reaction network involved in this operation will be truly impossible.

As far as the "prebioticity" of this material, one must carefully relate this property to the interaction between the organic matter produced in a more than plausible astrophysical scenario with an 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 knowledge of the primitive Earth [65] is entering a new phase where hypotheses about the nature of the early atmosphere and ocean on the Earth may be made in a more precise context. This will allow to study the interaction of some organics with a peculiar environment so that a phase space of parameters (T, pH, illumination . . .) may be explored using the semi-empirical approach of a non directed experiment. For example, the mechanism for formation of oligo-peptides [66, 67] that may be considered as, yet small, proto-proteins, provides a very useful framework to be tested in the laboratory. If such oligo-peptides can be synthesized by very natural processes in the laboratory, the route to PNA's (Poly-Nucleic-Acids) may be possible [68]. Such molecules are believed to be capable of some autocatalytic properties, thus defining a very "minimal" form of life (autocatalytic and heterotrophic capabilities), without yet considering any Darwinian type evolution which implies the building of a true genetic code, a task that remains inaccessible using this conceptual and experimental framework. However, 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 very early (pre)biochemical one.

5. CONCLUSIONS

Based on astronomical arguments i.e. the *availability* of the elements, due to their cosmic abundances *and* their physico-chemical properties, I point the fact that the basic elements for life supporting systems,

H, O, C, N, S and P, the ones that are present in DNA, cannot seriously be different elsewhere. Moreover, the very special chemical properties of carbon offer an extremely versatile and rich organic chemistry that is of considerable interest for life if associated with 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 early biochemical reactions. Recall that the number of minerals known to date is just around . . . 4500. Thus organic chemistry will provide a real continuum of species which must be at the heart of the Darwinian evolution. Indeed, if mutation, adaptation and selection are the most important characteristics of living systems, such a very progressive and small step by step evolution requires this chemical continuum to ensure that these three characteristics are always met.

Thus life based on very different mechanisms is highly improbable and the focus on the studies, connecting astrochemistry, complex organics that arise on extraterrestrial solids and end up in primitive oceans where prebiotic chemistry will start and may lead to the rise of the first biomolecular reactions, must be seriously considered. This field, accessible to experimentation, must be viewed as an interdisciplinary field strongly unified by cosmic evolution.

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