

Origins of life systems chemistry

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Abstract

By reconciling previously conflicting views about the origin of life – in which one or other cellular subsystem emerges first, and then ‘invents’ the others – a new *modus operandi* for its study is suggested. Guided by this, a cyanosulfidic protometabolism is uncovered which uses UV light and the stoichiometric reducing power of hydrogen sulfide to convert hydrogen cyanide, and a couple of other prebiotic feedstock molecules which can be derived therefrom, into nucleic acid, peptide and lipid building blocks. Copper plays several key roles in this chemistry, thus, for example, copper(I) catalysed cross coupling and copper(II) driven oxidative cross-coupling reactions generate key feedstock molecules. Geochemical scenarios consistent with this protometabolism are outlined. Finally, the transition of a system from the inanimate to the animate state is considered in the context of there being intermediate stages of partial ‘aliveness’.

Acknowledgements

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Trace the evolution of organic matter in interplanetary objects using residue analogues

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Abstract

This contribution focuses on one aspect of our work, which is related to the analysis of refractory residues formed from the UV irradiation and the subsequent warming-up to room temperature of astrophysical ice analogs, the RAHIA project. The understanding of the chemical composition of these refractory residues, commonly called “yellow stuff”, as well as the possible pathways to their formation in astrophysical environments, is an important step to establish what kind of organic matter could be available within interplanetary objects such as comets or asteroids, part of which end up as preserved meteorites on telluric planets.

1. Residue analogues for studying the chemical evolution in astrophysical environments

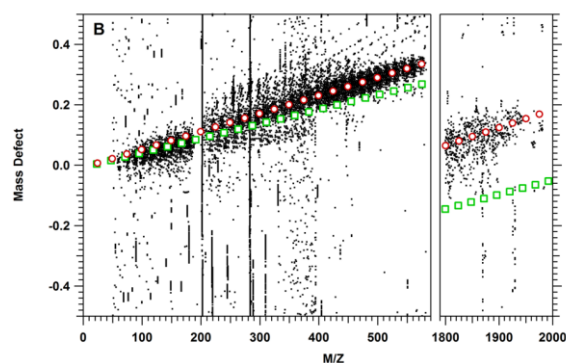


Figure 1. Mass defect vs. Exact Mass diagram corresponding to mass spectra of the ^{13}C residue analyzed in the negative ESI mode^[1].

We present here the first results obtained by spectrometric analysis with high resolution mass

spectroscopy (LTQ-XL-Orbitrap) of these residues^[1]. These analyzes show that residues are composed of thousands of molecules of high molecular weight ($m/z > 4000$), and present an average elemental composition $\text{H/C} = 1.6$, $\text{N/C} = 0.4$, $\text{O/C} = 0.4$ for an initial ice standard ice mixture, containing $\text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{NH}_3$ 3:1:1 (Figure 1).

We also develop specific data representation in order to obtain information on the residue composition^[2]. These representations allow to define that three different groups of molecules are present in these residues, molecules bearing only CHN, CHO or CHNO atoms. These representations also give important information on the family composition of each molecular group. All these developments will be used for the comparison of various residues as well as for the development of more specific analytical methods such as UHPLC-MS or GC-MS. These results demonstrate that from only three simple molecules CH_3OH , H_2O and NH_3 , a very complex chemistry occurs when these molecules are subjected to physical processes in the solid state such as those possibly present in the bulk of interstellar grains in the primordial molecular cloud at the time of the Sun formation and possibly then incorporated in comets and/or asteroids.

2. Residue analogue composition vs. meteorites

Furthermore we tentatively compare the abundance of the molecular families constituting our residue to molecules detected from meteorite analyses^[2]. Not so surprisingly, an excellent qualitative and semi-quantitative agreement is obtained between our residues and the soluble organic matter extracted from the Murchison meteorite, demonstrating that such residue can be used for tracing the chemical

history that leads to the formation of the organic matter found in meteorites for instance.

Acknowledgements

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Organic chemistry in the ionosphere of the early Earth

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Abstract

The emergence of life on the Early Earth during the Archean has required a prior complex organic chemistry providing the prerequisite bricks of life. The origin of the organic matter and its evolution on the early Earth is far from being understood. Several hypotheses are investigated, possibly complementary, which can be divided in two main categories: the endogenous and the exogenous sources. In this work we have been interested in the contribution of a specific endogenous source: the organic chemistry occurring in the ionosphere of the early Earth. At these high altitudes, the VUV contribution of the young sun was important, involving an efficient production of reactive species. Here we address the issue whether this chemistry can lead to the production of larger molecules with a prebiotic interest in spite of the competitive lysing effect of the harsh irradiation at these altitudes.

1. Introduction

1.1 Main composition of the early Earth

Recent geological studies inform us on the composition of the primitive atmosphere of the Earth during the Hadean and the Archean eons, before the rise of oxygen 2.5 Gyrs ago [1]. The atmosphere is now known to have been mainly composed of molecular nitrogen N_2 , carbon dioxide CO_2 and water vapor H_2O . Molecular hydrogen H_2 is moreover suggested as having been additionally outgassed from the mantle [2]. As the upper atmosphere is expected to be dry due to the cryogenic trapping in the troposphere, our study has been based on an atmosphere mainly made of N_2 and a few percents of CO_2 and H_2 .

1.2 Experimental simulation

To reproduce the organic chemistry which has been initiated by solar VUV photons in the ionosphere of the early Earth, we have used a plasma experiment. This is a Radio-Frequency Capacitively Coupled Plasma (RF CCP) at low pressure [3][4]. The characterization of the plasma discharge has been previously modeled and shows a maximum of the energy distribution at 600 nm and a tail with wavelengths down to 70 nm [5]. This similarity with the young Sun spectrum enables to simulate in the laboratory the energy deposition on the top of the early Earth atmosphere. The products are accumulated during the discharge by cryogenic trapping and are further analyzed by in situ mass spectrometry and mid-infrared absorption spectroscopy.

3. Results

CO_2 is found to be efficiently dissociated, with consumptions larger than 20%. It must be noted that CO_2 is the only source of carbon for organic chemistry in the present case. Hydrogen and nitrogen are also partially dissociated in the discharge even if in lower amounts than CO_2 .

The main product is carbon monoxide CO. However a strong coupling between the reactive species is observed through the productions of water H_2O , ammonia NH_3 , HCN and methanimine, $CH_2=NH_2$. Larger molecules are also detected in the gas products trapped and their identifications are in progress (Figure 1). Solid organic aerosols are finally collected showing that an efficiently organic growth is actually occurring in the discharge.

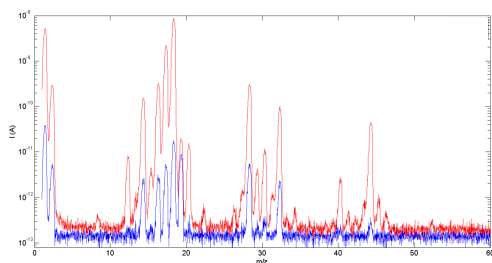


Figure 1: In blue, blank mass spectrum of the reactor. In red, mass spectrum of the products after 4 hrs of cryogenic trapping. M/z signatures are observed up to 60 u.

4. Summary and Conclusions

In the present experimental study we have simulated the chemistry occurring in the partially ionized ionosphere of the early Earth. We have chosen the extreme scenario of an oxidative atmosphere where carbon is only supported by carbon dioxide (no methane). The result is that we have not only observed prebiotic small bricks in the gas phase such as ammonia, methylamine and hydrogen cyanide, but also in the solid phase with the production of solid organic aerosols. This study confirms that the ionosphere could be an important source of prebiotic material, with a global scale on the early Earth. It would be responsible for the production of molecules with a prebiotic interest directly from the main atmospheric constituents, and their destruction under solar VUV irradiation would be prevented by the continuous conversion into solid organic aerosols.

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Starting life requires more than organic matter

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Abstract

A physicochemical approach is proposed to study requirements for the origin of life in agreement with developments made in Systems Chemistry for several decades. Emphasis is made on the occurrence of environments generating abiotic chemical systems making more of themselves under far from equilibrium conditions. It follows that the presence of organic matter is only one of the components needed for the process of chemical evolution leading to life. The presence of an energy source with a potential equivalent to that of visible light is needed to render the activation step kinetically irreversible and the reproduction loop a unidirectional flux of reactants. This condition is required in order that reproduction follows an exponential law and dynamic kinetic stability governs the evolution toward the selection of improved variants. According to these views, no fundamental difference can be found between the chemical and biological stages of evolution.

1. Introduction

Since the early mention of a “warm little pond” by Darwin, it is usually considered that the origin of life required liquid water, organic matter, and energy. Whether components of the first living organisms could be brought about by abiotic processes or produced through an early protometabolism directly connected to the origin of life triggered a lively debate. In a further stage, the emergence of life is sometimes considered as a matter of probabilities depending on the random emergence of the first self-reproducing polymer. However, organic components of life and especially polymers being thermodynamically unstable, free energy sources must be coupled to the process in order that the components of the first living organisms assemble. Therefore, the origin of life process could have unfolded under far from equilibrium conditions in accordance with an alternative approach taking into account one of the

essential features associated with life, namely disequilibrium. A subsequent issue is to determine more precisely how far from equilibrium the evolving system must be for expressing the possibility of selection of variants and further evolution towards complexity. Is there a threshold beyond which self-organization of life is possible? Or does the process simply need to be thermodynamically favorable? These questions are worth to be considered before assessing the ability of exoplanets to harbor life and its emergence.

2. Discussion

Though it gives some insight into the process through which life proceeds [1], [2], thermodynamics fails in describing the evolutionary aspects of life [3]. On the other hand, studies carried out since the seventies [4], [5] have shown the importance of replication and autocatalysis in chemical evolution. A condition for the selection of the most efficient variants through which a system can improve its dynamic kinetic stability [6], [7] lies in the occurrence of exponential growth that is only limited by the availability of reactants [8]. In agreement with the need of far from equilibrium conditions to observe self-organization through the development of dissipative structures [9], this requirement implies that the system must be fed with energy in a kinetically irreversible way. The requirement of kinetic irreversibility is associated with kinetic barriers high enough to avoid the reverse reaction corresponding to the activation step of a metabolic cycle or of a replication cycle (Figure 1). In other words, the reverse reaction must be negligible at the time scale (*i.e.* the generation time for reproduction) at which the metabolic cycle proceeds [10]. The main consequence of this requirement is that the process must not only be exergonic (correspond to a favorable free energy difference between products and reactants) but must additionally involve a cost of irreversibility corresponding to the kinetic barrier of the reverse reaction (Figure 1). This parameter corresponds to a

free energy threshold that must be passed in order that a behavior analogous to natural selection is observed [10]. Temperature and the turnover time of the metabolic or replicating cycle constitute the two parameters influencing this threshold. A value of ca. 100 kJ mol^{-1} can be assessed for this threshold at ambient temperature (300 K) and for turnover time values reproducing the lifetime of living organisms on the Earth [11]. This value represents a significant part of the free energy of covalent bonds in agreement with the specific ability of carbon in forming covalent bonds with other elements. It increases rapidly with temperature making the origin of life unlikely at high temperature [12]. Taking into account the need for biochemical energy carriers, a free energy potential equivalent to that of visible light has been assessed for energy sources needed to initiate the origin of life [10], [11]. Evolution has led to molecular engines capable of taking advantage of much lower potentials but these systems were not available for simple life occurring through chemical cycles.

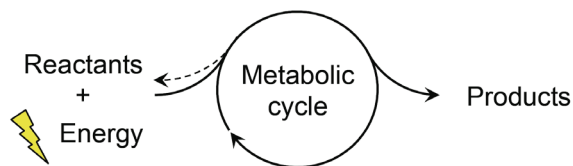


Figure 1: Kinetic irreversibility: the intermediates of a metabolic cycle must not revert to reactants (dashed arrow) within the timescale of the metabolic cycle.

6. Summary and Conclusions

A physicochemical analysis of life leads to the determination of energy requirements for the origin of life. The free energy threshold deduced from this analysis allows a selection among scenarios proposed for the origin of life. Energy sources possible for feeding rudimentary self-reproducing systems capable of evolution have thus been identified as photochemistry or other low entropy carriers. Hydrothermal systems miss the requirements in terms of chemical potential and chemical systems required for taking advantage of concentration gradients require highly sophisticated devices, the spontaneous emergence of which is in contradiction with the Second Law. This analysis is of high potential interest for determining conditions prone to the origin of life on planetary bodies.

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An introduction to the importance of organic matter evolution from the Interstellar medium to planetary systems

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Abstract

Most of the organic matter present in the Universe is formed and evolves in dense molecular clouds. During the evolution of grains, it undergoes many chemical changes (ion bombardment, UV irradiations, and thermal effect) to yield a highly complex organic matrix. The interstellar grains then form agglomerates found in small objects including the original organic matter (comets or asteroids). Next to endogenously formed organic matter, these small objects can serve as a reservoir of organic matter for the development of prebiotic chemistry on the surface of Earth-like planets. This kind of chemistry only developed in environments enabling the development of chemical networks continuously fed with matter and energy with a high enough potential. This is the prelude to the emergence of biosystems as it has indeed been the case on the Earth.

1. Introduction

A living organism arranges a set of chemical processes to maintain a non-equilibrium state by exchanging matter and energy with its environment, as well as to reproduce and evolve. A large set of molecules and a given environment therefore interact to sustain a living organism. The living cannot exist and grow without chemical processes, whereas a chemical reaction can take place without the necessity of living. Chemistry can be considered as "universal." However, clues that the emergence of life is a common and inevitable phenomenon in our Galaxy have not yet been provided. Currently, the known life forms reside only on the Earth. To determine if other planetary systems could undergo a similar evolution, it seems important to trace the fate of organic matter. This will help to understand what chemical processes could be established, in which environments and from which sources of matter and

energy ^[1]. The knowledge of this chemical evolution will provide clues about the possibility of finding other environments that may lead to the emergence of biosystems.

2. Astrochemistry: the evolution of organic matter in astrophysical environments

The chemical evolution begins in dense molecular clouds. These dense molecular clouds (10^3 to 10^5 molecules of hydrogen per cm^3) are formed of gas and dusts. Dusts are formed of a cold core (10 to 50 K) of refractory silicates and/or carbonaceous material surrounded by a set of molecules forming an icy mantle. These interstellar ices are mostly formed of water, methanol, carbon monoxide, carbon dioxide, ammonia and organic molecules such as formaldehyde and urea. These interstellar grains are of considerable importance in the process of chemical evolution of the interstellar organic matter, because the formation of the ice allows the concentration of organic molecules at the surface of grains, which facilitates the reactivity and the chemical evolution of the original organic matrix ^[2]. In some areas, the dense molecular cloud can collapse leading to the formation of proto-stars. This proto-star evolves and emits various types of radiation interacting with the proto-stellar envelope, where interstellar grains are present. These radiations (ultra-violet, infrared...), associated with cosmic rays (energetic charged ions) alter the molecules constituting ices, driving the organic matter towards a higher complexity. Thereafter, the altered interstellar grains are involved in the constitution of a proto-planetary disk. Depending on the grain position relative to the proto-star, the organic matter can continue to evolve through various physical and chemical alterations that proceed along with the

formation of a planetary system such as the Solar System.

3. Prebiotic chemistry: the evolution of organic matter in specific environments

Once the planetary system is stabilized, two reservoir of organic matter can be distinguished. Organic matter of exogenous source can be delivered to the surface of the terrestrial planets by the impact of comets, asteroids and interplanetary dust ^[3]. Atmospheric and geochemical processes can also form organic materials endogenously ^[4].

The emergence of biochemical systems can be understood as resulting from the development of more complex chemistry under the chemical and physical conditions of the environment. This transition requires the emergence of molecular entities or reaction networks able to reproduce themselves and then to take advantage of the specific kind of stability associated with things that can be replicated ^[5]. This kind of prebiotic chemistry could only develop in specific environments, where physical and chemical conditions can maintain a dynamic chemical networks in a far from equilibrium state by constantly feeding the system with matter and energy. This transition occurred on the early Earth but we have no indication that a tightly defined environment is required. In the mean time, there is no basis for speculations that exogenous environments rich in organic matter may also lead to an emergence of life. The presence of organic matter itself is not sufficient. As noted above, the environment must provide free energy with a potential (150 kJ.mol^{-1}) sufficient to enable the development of a far of equilibrium chemical network undergoing self-organization. Consequently, the use of the term "prebiotic", with the meaning "closely preceding the emergence of life" to qualify these environments, should be restricted to the ones in which free energy with a high potential is present. It should not be applied to astrochemistry as a whole, unless a sufficient amount of energy is available.

4. Conclusion

The studies on the chemical evolution in astrophysical environments have demonstrated that organic matter is formed abiotically, destroyed and

available everywhere in the Universe, in more or less complex forms. Carbon, hydrogen, nitrogen and oxygen tend to develop spontaneously a chemistry that is universal and not limited to the biochemistry of living organisms. However, the presence of organic matter in various astrophysical environments is not sufficient for the emergence of life. Only astrophysical environments presenting a specific set of physical and chemical conditions enabling the development of far-from-equilibrium processes will enable the self-organisation of organic matter towards the living state. For understanding where life can arise, we have to understand which environments could gather these conditions.

Acknowledgements

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Life Origination Hydrate Theory (LOH-Theory): natural gas and niter as sources of amino-acids and proteins in the process of living matter origination

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Abstract

Not only DNAs, but amino-acids (AAs) and proteins can be obtained from natural gas, niter and phosphate.

1. Introduction

We proved earlier (e.g., [1–4]) that nothing put obstacles in the way of DNA formation from niter, CH₄, and phosphate in the CH₄-hydrate honeycomb structure. Only three sets of these reactive molecules should meet together under definite conditions in any localization in order that a great number of different DNAs should be produced. The probability of such an event is increased by the fact that CH₄ is localized and, thus, only two sets of molecules should enter into the first set, by the fact that Nature as if foresaw in advance such a possibility and had created a hydrate matrix to make possible formation of the non-trivial DNA structures, and by the fact that It harmonized the conditions of existence of the matrix structure with the conditions when the source substances are reactive and, thus, had prepared in advance all necessary conditions for creation, in different CH₄-hydrate localizations, of multitudes of polymer DNA molecules identical in their polymer chains and in elemental composition but different in the sequence of the arrangement of quite definite side functional groups. But how did Nature contrive to form AAs and proteins? OK, maybe, some of them could originate from CH₄ and niter molecules (we will show that this is so). But what is about the S-containing AAs? Indeed, any S-containing substance represents the fourth source substance, but no “rendezvous” of four sets of different molecules in any localization is possible according to the probability theory and Boltzmann equation. However, Nature took care of this as well. Indeed, natural gas contains not only CH₄ but frequently implies H₂S, COS, and CH₃S [5] and, in our theory, only three substances should meet together to give living matter.

2. Could natural gas and phosphate be precursors of AAs and proteins?

We analyze here some examples showing that the answer to the question of the title of this section is positive. In the lecture, all AAs will be considered.

Let us consider the following reactions:

- (1) $2\text{CH}_4 + 1.5\text{KNO}_3 = \text{Gly} + 1.5\text{KOH} + 0.5\text{NH}_3 + 0.5\text{O}_2$;
 - (2) $3\text{CH}_4 + 2\text{KNO}_3 = \text{Ala} + 2\text{KOH} + \text{NH}_3 + \text{O}_2$;
 - (3) $5\text{CH}_4 + 3\text{KNO}_3 = \text{Val} + 3\text{KOH} + 2\text{NH}_3 + 2\text{O}_2$;
 - (4) $5\text{CH}_4 + 2\text{KNO}_3 + \text{H}_2\text{S} = \text{Met} + 2\text{KOH} + \text{NH}_3 + 2\text{H}_2\text{O} + \text{H}_2$
 - (5) $4\text{CH}_4 + \text{KNO}_3 + \text{CH}_4\text{S} = \text{Met} + \text{KOH} + 4\text{H}_2$
- for syntheses of glycine H₂NCH₂COOH (1), alanine CH₃CH(NH₂)COOH (2), valine CH₃CH(CH₃)CH(NH₂)COOH (3), and methionine H₃CSCH₂CH₂CH(NH₂)COOH (4) and (5).

For each of these reactions, the standard Gibbs free energy changes are negative, and for reactions (1)–(5) $-\Delta G_j^0$ (kJ/mol) = 251.0, 200.1, 118.6, 496.6, and 95.9, respectively. These magnitudes are so high that there are no doubts that, under the conditions of the CH₄-hydrate existence, all equilibria are right-shifted. Analogous results are obtained for other AAs. The ΔG_j^0 values are calculated on the basis of [6, 7]. It is known that CH₄ is capable of reacting with NO₃[−]-ions at 270–290 K (Konovalov’s reaction); the process is slow but Nature is never in a hurry. We would remind to our riders one more indisputable fact, which is regarded by us as a rather important one when considering the mechanism of living matter origination: natural gas and niter is the unique pair of minerals capable of giving all organic components of DNAs and all AAs; no other such a mineral pair exists. Consider now briefly whether peptide formation from AAs proceeds with a decrease in the Gibbs free energy. Peptides can be considered as the 3D-polymers composed of AAs bound to each other with the peptide bonds (Figure) formed by α-carboxyl- and α-amino-groups of the adjacent amino-acidic radicals. Notice that the observations of the processes that proceed within living cells of the present organisms

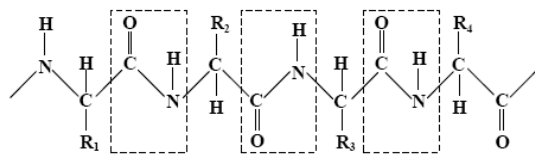


Figure: Fragment of a peptide polymer chain: R_i are radicals, and the rectangles show peptide bonds.

help us to understand the mechanism of living matter origination, because the intracellular processes have a number of common features with the processes of formation of cells in the primary super-protoplasm [8] obtained after liquation of the parental gas-hydrate structures. Proteins form through reactions of AAs polycondensation. The available thermodynamic data on the reactions of such a type are technically questionable. Therefore, we use the following simple logical consideration which shows that the reactions of such a type proceed with a decrease in the Gibbs free energy. The Gibbs free energy of any substance under any fixed conditions doesn't depend on the way of production of this substance. Let substances A and B be incapable of interacting with each other with formation of C under some conditions, i.e., the Gibbs free energy change for their problematic interaction with production of C be positive. Then, the substance C, being produced under some other conditions by any method and then being returned to the conditions under which it can't be produced, would be thermodynamically unstable and, under thermodynamic equilibrium, should transform into A and B. Meanwhile, different proteins exist really in the composition of living matter; therewith, 20 so-called proteinogenous AAs are in the protein compositions and some of them are also in the composition of protoplasm and the others are in the protein composition only. This phenomenon is observable under all conditions when living matter exists, including under underground ones similar to the conditions when original living issues had formed. This fact counts rather firmly in favor of conclusion on the negative $\Delta_f G^0$ values for the reactions of condensation of AAs with formation of peptide bonds. The $\Delta_f G^0$ magnitudes can be small (protoplasm contains the corresponding AAs) or rather large (protoplasm contains no corresponding AAs) depending on the specificity of the protoplasm composition, which is associated with the mitosis steps. Notice that no kinetic delay should determine the equilibrium. Indeed, it is well known that a temperature increase or an acidity change leads to protein hydrolysis; in other words, the protein-protoplasm equilibrium becomes established rather

quickly. The equilibrium is mobile, but all events of normal life processes are based on the repetitive oscillations near the equilibrium conditions, which depend on the ambient conditions and intra-cellular state. In our opinion, the primary proteins originated just through polycondensation of AAs and the above consideration is important for understanding the mechanisms of the living matter primary formation and subsequent extended reproduction.

3. Conclusion

Origination of AAs and proteins under the conditions, which arose after liquation of gas-hydrate systems filled with DNAs after their formation from CH_4 , niter, and phosphate in CH_4 -hydrate localizations, were thermodynamically possible and kinetically realizable on the basis of natural gas and niter.

Acknowledgements

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Hydrothermal alteration experiments: tracking the path from interstellar to chondrites organics

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Abstract

Organic molecules are detected in primitive carbonaceous chondrites. The origin of these organics, whether formed prior the accretion phase, or in-situ on the parent body, is still a matter of debate. We have investigated experimentally the chemical evolution of interstellar organic molecules submitted to hydrothermal conditions, mimicking asteroidal alteration ($T < 200^{\circ}\text{C}$). In particular, we want to assess the potential catalytic role of clays minerals in the polymerization/degradation of organics. Hexamethylenetetramine (HMT, compound of C-N bonds) is used as a plausible interstellar precursors from icy grains. Experimental products reveal a large diversity of molecules, including nitrogen organic molecules similar to those found in chondrites.

1. Introduction

Organics are widely observed in astrophysical environments, including in molecular clouds, circumstellar envelopes and protoplanetary disks [1]. Astronomical observations of the gas phase show a rich diversity of mainly small molecules (up to 10 atoms), while the composition of the solid phase remains cryptic due to limitations of infrared spectroscopy. Still, the solid phase, composed of dust and icy grains, is supposed richer in complex organic molecules. Laboratory experiments have been performed in an attempt to reproduce processes occurring during stellar formation (UV photolysis, heating effect) affecting these icy grains initially composed of H_2O , CO_2 , CO , NH_3 , CH_3OH . These experiments yield an organic-rich residue at room temperature, where the hexamethylenetetramine (HMT, $\text{C}_6\text{H}_{12}\text{N}_4$) may constitute more than 50wt% of the total organic residue [2-3]. Experimentally formed in ice from ammonia and formaldehyde [4], HMT has not yet been detected. However, asteroids may have accreted this molecule, and many other formed in icy grains, as primitive constituents.

Asteroids, thought to be meteorites' parent body, are initially formed from icy grains, dust, minerals, and organic molecules sampled in the protosolar nebula [5]. After accretion, parent bodies have all experienced hydrothermal (aqueous) alteration and/or thermal metamorphism at varying degrees. Regarding hydrothermal alteration, the mineral assemblages of meteorites (such as phyllosilicates and carbonates) have recorded these alteration episodes and reveal crucial information regarding the meteorite history. Among meteorites, carbonaceous chondrites are the richest in organic matter, and thus constitute the best targets available to investigate the origins of organics in our solar system [6]. Yet, discriminating the alteration molecular signal from the original molecular signal, i.e. rigorously constraining the impact of hydrothermal alteration on organics, remains highly challenging.

2. Experimental hydrothermalism of interstellar molecules

Two synthetic (organic free) clays minerals comparable to chondritic clays have been selected for our experiments: Na^+ montmorillonite and Fe^{3+} nontronite. Experiments have been conducted at low temperatures ($< 150^{\circ}\text{C}$), under relatively low pressure (only induced by water liquid/vapor equilibrium), and in an alkaline pH solution to properly mimic processes occurring on asteroids. The impact of the presence of additional molecules such as short carboxylic acids (detected in astrophysical environments) have also been investigated.

On figure 1 are reported the gas-chromatographs of an HMT solution and a mixture containing HMT and carboxylic acids after having been submitted to hydrothermal conditions without mineral during 18 days at pH 10. Thanks to GC-MS, we can identify several new compounds after hydrothermal alteration of HMT, such as methyl pyrazole/imidazole

derivatives, methyl pyridine/pyrazine derivatives and many other cyclic nitrogen, up to m/z 254. In the presence of short carboxylic acids, amides are produced (red pics between 4 and 10 min.), including formamide derivatives, while less cyclic nitrogen species are produced.

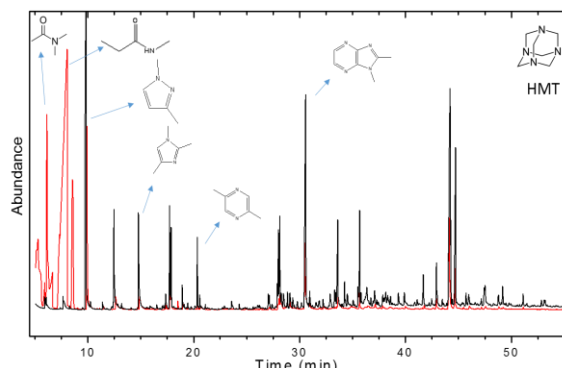


Figure 1. GC Chromatograph obtained from the mixtures after hydrothermal alteration (18 days of at 150 °C, pH 10), in black from HMT solution and in red from HMT+carboxylic acid mixture. (HMT structure is in the right corner.)

On figure 2 are shown the FTIR spectra of solid phases from mixtures of HMT and nontronite recorded before and after having been submitted to hydrothermal conditions during 18 days at pH 10. While no organic signature can be observed with the nontronite before the experiment, absorption features indicating the presence of organics (1400, 1700 and 3300 cm^{-1}) can be noticed after the experiment. The increase of the interlayer spacing of the clay mineral after these experiments, revealed by XRD data, suggests that these likely newly formed organics are trapped within the nontronite interlayers. The same observations have been done with montmorillonite clay and from other solutions of HMT with carboxylic acids.

3. Conclusions

Our study reveals that organic molecules may undergo complex chemical transformations during hydrothermal alteration. In the absence of minerals, HMT leads to many nitrogen cyclic compounds and to amides, which could further evolve into nucleobases or amino acids species. Things appear a bit different in the presence of clays that may trap newly formed organics and thus protect them from subsequent alteration.

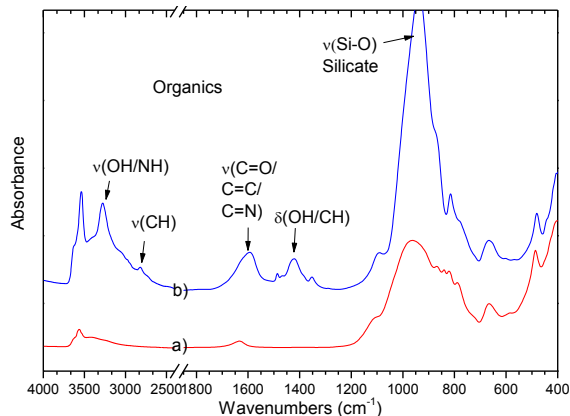


Figure 2 Infrared spectra of a) nontronite before experiment, b) after aqueous reaction with HMT solution, at 150 °C, alkaline pH, during 18 days.

These studies are relevant for understanding the evolution of the organic matter within asteroid and to access its origins.

Acknowledgements

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Glyceraldehyde and glycolaldehyde in interstellar ice analogues and the role of aldehydes in cosmochemical evolution

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Abstract

Our understanding of the molecular origin of life is based on amino acids, ribose, and nucleobases that – after their selection by prebiotic processes – initiated the evolutionary assembly of catalytic and informational polymers, being proteins and ribonucleic acids. Following previous amino acid identifications in the room-temperature residues of simulated circumstellar/interstellar ices [1,2] we have searched for a different family of molecules of potential prebiotic interest. Using multidimensional gas chromatography coupled to time-of-flight mass spectrometry, we have detected ten aldehydes, including the sugar-related glycolaldehyde and glyceraldehyde – two species considered as key prebiotic intermediates in the first steps toward the synthesis of ribonucleotides in a planetary environment.

1. Introduction

Amino acids, sugar-like molecules, and nucleobases have been detected in exogenous samples of carbonaceous chondrite meteorites and also in interstellar ice analogues. Glycine was identified by the help of the Stardust mission in a sample of comet 81P/Wild 2. Recently, experimental evidence was given, revealing that the origin of ribonucleotides bypassed the classical chemical synthesis and proceeded from the starting materials glycolaldehyde and glyceraldehyde via pentose amino-oxazolines [3]. Analogously, meteoritic amino acids were suggested to originate from aldehyde precursors in a manner that chiral aldehydes stereo-dictated the chirality of meteoritic amino acids [4]. Despite of the importance of aldehydes in ribonucleotide evolution and amino

acid handedness, pre-biotic aldehyde intermediates escaped so far direct systematic detection due to their chemical reactivity and instability. Here we report the detection of aldehydes including glycolaldehyde and chiral glyceraldehyde (Figure 1) in the room-temperature residue of an interstellar ice analogue that was ultraviolet-irradiated in a high vacuum at cryogenic temperature.

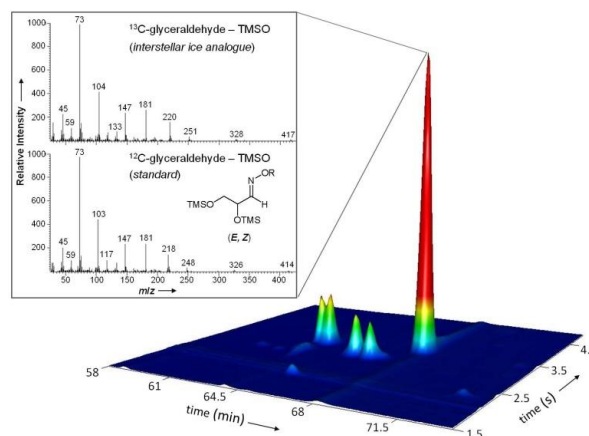


Figure 1: Glyceraldehyde detected in simulated cometary matter. Identification of glyceraldehyde as O pentafluorobenzyl oxime (R) trimethylsilyl ether (TMSO) in simulated cometary ice residues using multidimensional gas chromatography. The corresponding external glyceraldehyde standard shows identical retention times and logically ^{12}C isotopic signatures in its mass spectra. The mass fragmentation reveals that glyceraldehyde formed in the residue is entirely composed of ^{13}C -isotopes provided by the $^{13}\text{CH}_3\text{OH}$ reactant present in the original interstellar ice mixture.

2. Results

We used new multidimensional gas chromatography coupled to time-of-flight mass spectrometry for the detection of ten different aldehydes [5]. Some of the identified aldehydes are also found in cometary ices. Chiral implications in the photochemical generation of glyceraldehyde in the ice samples are of special interest since this process could proceed through a formose-type reaction process with autocatalytic feedback and possible asymmetric amplification. In this context the chiral glyceraldehyde was subjected to anisotropy spectroscopy [6] revealing high anisotropies which make this aldehyde a suitable recipient for the chirality of circularly polarized light. Our results show that the spontaneous generation of aldehydes in the interstellar medium is possible, allowing to understand intermediate steps in chemical evolution towards enantioselective amino acid and ribonucleotide formation.

3. Perspectives

The reported identification of aldehydes is of importance for two reasons: This identification allows for a better understanding of the origin of biomolecular asymmetry in the context of asymmetric ribonucleotide synthesis and in the context of asymmetric amino acid synthesis. Furthermore these results help in the ongoing data interpretation of the Rosetta mission that landed on a cometary nucleus on 12 November 2014 [7,8] to perform in-situ measurements of cometary ices, particularly with the COSAC instrumentation which contains a GC-MS device specifically designed for the characterization of organic molecules [9].

Acknowledgements

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Sublimation of mixtures of α -alkyl amino acids for enantioenrichment.

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Abstract

High temperature sublimations of mixtures of α -alkyl amino acids with, at the minimum, one enantioenriched component allow huge enantioenrichments of the previously racemic or enantioenriched components.

1. Introduction

Recent studies on low or high temperature sublimations of scalemic mixtures of natural amino acids (AAs) highlighted unexpected enhancements of enantiomeric excess (ee) [1-5]. We have investigated systematic studies on the high temperature sublimation of mixtures of mono-alkylated AAs in the aim of rationalizing their properties in this phase transition and to precise the potentialities of the sublimation for enantioenrichment in Astrobiology.

2. Results and Discussion

Subliming at very high temperature (490°C), in a closed cell, mixtures of a racemic AA in the presence of an enantiopure leads the deracemization of the former.

Using one enantiopure and an AA with various ee, an increase for the latter of the ratio between the enantiomer of the same handedness than the one of the enantiopure and the other one was systematically observed (Fig.).

Thus, when one enantiopure (Val) and leucine with ee ranging from 95 % (D) to 95 % (L) were sublimed together, this behavior was observed leading in some cases to a switch of the handedness of leucine. As

typical examples, starting from L-Val and 40 % D-Leu in a 4:1 ratio, a 20 % ee of D-Leu was obtained after sublimation. In the same conditions, with a 10% ee (D)-Leu, a 20 % (L)-Leu was obtained.

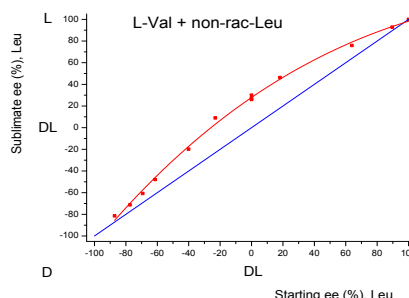


Fig. High temperature sublimation of L-Val (1 equiv.) with Leu (0.25 equiv.).

Using one enantiopure AA and racemic AAs, a strong synergistic effect was evidenced for the most complex mixtures (Table). The efficiency of the sublimation is dependent - on the presence of a gas in the cell and on the nature of the gas - on the temperature of sublimation - on the nature of the amino acids since good results were only observed with 1-alkyl derivatives.

This effect was still observed starting from one enantioenriched AA and racemic AAs. In this case, all the AAs of the starting mixture are enantioenriched after sublimation [7].

Table. High Temperature Sublimation of mixtures of one enantiopure and several racemic amino acids.

Condition	Starting mixture (equiv.)	Sublimed mixture (ee %)
490°C, air, 3 AAs	L-Leu + DL-Ala + DL-Val 1:0.25:0.25	L-Leu: 99.5; L-Val: 52; L-Ala: 53.1
490°C, air, 6 AAs	L-Val + DL-(Ala, Leu, 2-ABA, norVal, isoLeu, norLeu) 1:6x0.25	L-Val: 100; L-Ala: 50.0; L-Leu: 41.5; L-2-norVal: 55.3; L-norVal: 42.0; L-isoLeu: 20.4; L-norLeu: 39.4
490°C, air	L-Val + DL-Ala + DL-Leu 1:0.25:0.25	L-Val: 100; L-Ala: 49.6; L-Leu: 36.4
420°C, air	L-Val + DL-Ala + DL-Leu 1:0.25:0.25	L-Val: 100; L-Ala: 13.8; L-Leu: 12.5
390°C, air	L-Val + DL-Ala + DL-Leu 1:0.25:0.25	L-Val: 100; L-Ala: 2.5; L-Leu: 1.5
490°C, N ₂	L-Val + DL-Ala + DL-Leu 1:0.25:0.25	L-Val: 96.0; L-Ala: 11.6; L-Leu: 17.7
490°C, NO	L-Val + DL-Ala + DL-Leu 1:0.25:0.25	L-Val: 99.8; L-Ala: 55.4; L-Leu: 53.4
490°C, CO ₂	L-Val + DL-Ala + DL-Leu 1:0.25:0.25	L-Val: 99.5; L-Ala: 22.2; L-Leu: 24.6
490°C, vacuum	L-Val + DL-Ala + DL-Leu 1:0.25:0.25	L-Val: 100; L-Ala: 3.0; L-Leu: 7.1

6. Summary and Conclusions

The sublimation has been more than under-investigated in Astrobiology. We and some others have already showed that a partial sublimation at low temperature of enantioenriched compounds gives sublimates or residues which can be highly enantioenriched in function of the studied compound and the ee(s) of the starting material. However, segregation of enantiomers gives an ambiguous answer for the origin of homochirality on the Primitive Earth since it has to be explained why only the enriched sample is reacting in the following steps. The selective decomposition of one enantiomer or the racemization of the minor enantiomer into the major

one is much more convenient to explain a chemistry based on one kind of enantiomers.

Up to date, only the amino acids contained in meteorites give an answer for the first imbalance between enantiomers. Many other syntheses have produced huge amounts of racemic amino acids on the Primitive Earth. With such small enantiomeric excesses for some amino acids, to determine the way for enantioenrichment is really challenging. The main advantages of our approach are the use of any complex mixture of 1-alkylated amino acids and drastic conditions compatible respectively with the organic syntheses occurring four billions years ago and the warm surface of the Young Earth subjected to frequent meteorite bombardments and to lava flows. Since its effectiveness is enhanced for complex mixtures, multiple high temperature sublimations in a large range of temperatures could be the key of huge enantioenrichments of several monoalkylated α -amino acids on the Primitive Earth at the early stage of the chemical evolution and just after the formation of amino acids.

Acknowledgements

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From Astrochemistry to Astrobiology: a methodological approach

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Abstract

Astrochemistry is a well-established discipline of astrophysics devoted mainly to the chemistry that is observed in the interstellar medium. Complex organic molecules are found in many different environments, mainly in molecular clouds in star forming regions. However, it is not clear if these molecules, often presented as prebiotic, are indeed involved in the process leading to life emergence on a planet. Based on astronomical arguments and on different laboratory experiments aiming at the simulation of interstellar ices, we examine the possible connection between astrochemistry and astrobiology.

1. Introduction

Solid state matter in astrophysical environments evolve in a cyclic manner. Heavy elements are produced in the nucleosynthetic processes within stars. They are ejected in space by the explosions of supernovae of massive stars. The interstellar medium is thus enriched in these elements and this astration process will lead to the universal (at least in our local interstellar medium) consequence that the relative abundances of the elements are described by the so-called cosmic abundances, well measured in the atmosphere of the Sun or in primitive chondrites. These cosmic abundances represent a very strong constraint for astrochemistry.

1.1 Grain formation processes

Solid state materials such as interstellar grains are observed to be formed in the atmospheres of late type stars, red supergiants in their AGB phases. These grains are of a mineral nature (eg silicates) or pure

carbon, depending on the O/C ratio of the envelope where they are formed. Although nucleation and condensation are processes that are difficult to fully apprehend, the composition of these grains are usually correctly described, to the first order, by a condensation sequence at equilibrium that considers the formation of different minerals according to their thermodynamic properties (their enthalpy of formation).

1.2 Observed depletion of the elements

As is well known, cosmic abundances of the elements are not observed on lines of sight to distant stars: some elements are depleted. They are missing from the gas phase essentially because these elements, the more refractory ones, are blocked in the interstellar grains. Some elements are not depleted at all (N, S, P), others only mildly (O, C) while minerals-constituting elements (Si, Al, Fe, Mg, Ca) are heavily depleted (2 to 3 orders of magnitude).

1.3 Astrochemical evolution

The first obvious consequence of this grain formation process is that, since H, O, C, N, S (and P?) are abundant and present in the gas phase, these elements will display essentially an organic chemistry that is largely observed through radio-astronomy in the sub-mm and mm ranges. Furthermore, as noted very early by Oort and van de Hulst [1], gaseous elements that are cosmically abundant and remain in the gas phase of the interstellar medium will, together with hydrogen atoms, form simple hydrides (H₂O, CH₄, NH₃) and, in the presence of cold surfaces, vast amounts of ices will result. These ices are indeed observed by infrared spectroscopy; they are well documented and reflect the interplay between gas

phase chemistry (ion-molecule reactions for example) and cold solid surfaces where ices can form, stabilize and offer the possibility to develop more chemical complexity.

1.4 Natural evolution of the ices

Astrophysical ices will follow a complex pathway that is related to the evolution of the molecular cloud leading to the formation of protoplanetary disks. Ices will get photo- and thermo-chemically processed and, because of the natural protection offered by the presence of the grain surfaces and their shielding, molecular complexity and the formation of very complex molecules is expected. This evolution is difficult to follow from observations essentially because infrared spectroscopic features are hidden by the most abundant species (H₂O). However, laboratory simulations are possible and present a global view to this molecular complexity.

1.5 Laboratory simulations

Laboratory simulations of the photo/thermo-chemical evolution of ices are relatively easy to perform in the laboratory using classical methods inherited from *Matrix Isolation Spectroscopy*. A gas mixture made of the most abundant observed IS molecules is deposited onto a cold (10 to 77 K) window and irradiated (in our case by UV photons). Heating the sample to room temperature always leads to the formation of a very complex organic residue that can be analysed by different methods from analytical chemistry techniques (gas chromatography coupled to mass spectrometry and/or Very High Resolution Mass Spectrometry techniques such as Orbitrap). The first method reveals the presence of many specific compounds such as amino-acids [2] and sugars [3] that may be related to prebiotic chemistry although the direct connection is not yet firmly established. The second method shows the obtained complexity: thousands of molecules are detected starting with a mixture containing only three simple ones [4]

1.6 The methodological approach

The extreme complexity of the organic residues produced by the simulations shows that a classical approach involving a full reductionist understanding of the formation of these species is clearly impossible. Non-directed experiments performed in the

laboratory do represent the only possible solution to this problem. Tentative comparisons between this obtained complexity and the one observed in meteorites are underway and show that our approach, considering these organic residues as templates for this complex extraterrestrial chemistry offers some validity that needs to be seriously taken into account.

2. Summary and Conclusions

Astrochemical evolution, following the evolution of our Galaxy, clearly favours the emergence of a complex organic chemistry. The role of cosmic ices in this evolution toward complex organic matter can be simulated in non-directed laboratory experiments. However, the prebiotic nature of this matter and its role in prebiotic chemistry at the surface of a planet is far from being understood. Other non-directed experiments should be performed considering the interaction of these materials with the primitive environments offered by planets such as the Earth.

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