

prebiochem : CECAM Workshop "Atomistic simulation in prebiotic chemistry: a dialog between experimentalists and theorists"

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Abstracts of oral presentations:

The organic content of comet 67P/Churyumov-Gerasimenko as revealed by the Rosetta mission.

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Comets contain a large number of organic molecules: they are the small bodies of the Solar System with the highest content in carbonaceous matter explored to date. Since the comet 1P/Halley exploration era in 1986, a broad diversity of volatile compounds have been detected in their atmosphere, and the dark color of their nucleus is often regarded as a sign of the presence of complex carbonaceous material.

Not only the nature and amount of organic matter in comets could have played a crucial role in the origin of life on Earth, but they also most certainly point towards the physicochemical processes that were prevailing at the time of their formation in the protoplanetary nebula, or even before if comets have incorporated to some extent material directly inherited from our native molecular cloud.

The exploration of comet 67P/Churyumov-Gerasimenko (67P) by the Rosetta spacecraft between 2014 and 2016 has considerably expanded our knowledge about the composition of comets. The details of the organic content of comet 67P are progressively revealed by the complementary measurements of ROSINA, VIRTIS, COSAC, PTOLEMY, and COSIMA instruments. Almost three years after the end of the mission, we will make an inventory of the organic molecules that have been identified during the operations at the comet, both in the gaseous phase or as a dust component, and derive a carbon budget in the nucleus. What was expected and observed, unexpected and found, and also what was expected but not seen, are keys for a consistent scenario about the origin of the organic matter in comet 67P and how it has been incorporated into the nucleus. The nature of the volatile compounds in their broad diversity observed in the gaseous phase, and the macromolecular organic material dominating the refractory component, seem to point to distinct sources of organic matter that were incorporated into the nucleus of the comet when it formed some 4.5 billion years ago. The relevance of this organic mixture will be discussed in the context of astrobiology.

The role of gas-phase reactions in prebiotic chemistry

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In the sequence of steps which are believed to have led from elementary particles to the emergence of life, an important one is the formation of relatively complex organic molecules from the simple parent species abundant in space. The accumulation of organic molecules of increasing complexity, indeed, is accepted as an important stage preceding the appearance of the first living organisms. But how massive organic synthesis could occur in primitive Earth, i.e. a water-dominated environment, is still a matter of debate.

The aggregation of H, O, C, N and other atoms into molecules and their subsequent chemical evolution are occurring also now in the Universe, as witnessed by the identification of ca. two hundred gaseous molecules in the interstellar medium, including also species with a prebiotic potential (e.g. formamide and glycolaldehyde). The possible link between those prebiotic molecules synthesized in space and the appearance of life on Earth is not only interesting per se, but it might offer exciting support to the conjecture that life is a widespread phenomenon in the Universe, rather than a local, fortuitous case. The processes leading to interstellar prebiotic gaseous molecules under the harsh conditions of interstellar objects are far from being understood. Most current astrochemical models privilege grain-surface chemistry because gas-phase chemistry is not believed to have the capability of leading to complex species. In this scenario, grain-surface chemistry is not only responsible for the formation of hydrogenated molecules during the pre-collapse phase, but also for the whole set of the observed organic molecules. Nevertheless, as recently pointed out by experimental and theoretical work on several gas-phase reactions [1,2,3], many gas-phase routes have actually been overlooked, while their inclusion in the astrochemical models with the parameters determined in laboratory experiments or via accurate theoretical calculations could be decisive in reproducing the observed abundances of prebiotic molecules. In this talk, the status of our knowledge of interstellar gas phase chemistry will be addressed. Several reactions that are believed occur in the upper atmosphere of Titan will also be noted [4].

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The Formamide model

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When the first study on the role played by mineral catalysis in the thermal oligomerization of formamide was published about 20 years ago, the possible future for this reaction in prebiotic chemistry was not yet clear [1]. Today we know that formamide is a very effective chemical precursor, widely distributed in the Cosmos, capable of producing a very complex multi-component chemistry in the frame of the chemiomimesis concept [2]. The nucleic acid bases, amino acids, carboxylic acids possible intermediates of pre-metabolic cycles, sugars and membrane surfactants, are formed in large variety from formamide, and formamide/water mixture, in the presence of terrestrial and non-terrestrial minerals and of different forms of energy [3-4]. Complex nucleoside derivatives have been also obtained simply by irradiating the formamide with proton beam in the presence of meteorites [5]. Insights on the mechanism of the formamide oligomerization have been reported, indicating the possibility of unique reaction pathways to obtain a large panel of nucleic acid bases and amino acids [6]. In this presentation we will discuss some of the results already acquired in the light of new prebiotic scenarios in which the chemistry of formamide is translated from general reactivity models to more specific planetary geochemical models, such as the serpentinization reaction [7].

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Contribution of charged particles to the organic growth in the upper atmospheres of Titan and the Early Earth

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From the recent Cassini-Huygens space mission we learned that ion-chemistry was a strong promoter of organic chemical growth in the upper atmosphere of Titan. Positive and negative organic ions were detected with masses up to several thousands mass units [1]. This chemistry is far from being totally understood, and has also been recently proposed as a possible contributor to prebiotic chemistry on the early Earth. Laboratory experiments are being developed to complete and understand these original pathways towards chemical complexity. In LATMOS we built an experimental platform using plasma [2] and far-UV techniques [3] to simulate the chemistry occurring in upper planetary atmospheres. These reactors are coupled to in situ mass spectrometry diagnosis to characterize the contribution of positive and negative ions to the global chemical network. We will present our results on the case of Titan and proxy for the early Earth atmosphere [4][5].

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Electrophilic Aromatic Substitution: from the Isolated Reactant Approach to Solution Phase Simulations to probe Chemical Reactivity

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Atomistic simulations are an extremely valuable tool in the study of chemical reactivity. In this lecture, I will discuss the assessment of chemical reactivity in a cornerstone reaction from organic chemistry, the electrophilic aromatic substitution. In a first part, reactivity and selectivity is discussed using properties of the isolated reactants through reactivity indices from the so-called “Conceptual DFT”. Next, ab initio atomistic simulations in solution phase will be used to explore different reaction mechanisms. In a final part, the mechanism is investigated from a qualitative Valence Bond perspective.

Glycine Condensation Chemistry Under Extreme Conditions

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Polypeptide synthesis in prebiotic environments is thought to be a pathway for the formation of more complicated molecules needed for the origins of life. Condensation reactions involving the simplest protein forming amino acid glycine serve as an important model for understanding the formation of more complicated polypeptides and proteins. One possibility for the formation of polypeptides or precursor molecules on early Earth is under extreme temperatures and/or pressures. Extreme conditions are a known means to access otherwise unlikely and slow chemical synthetic routes and can prompt the formation of new and exotic products and phases. This could have conceivably involved cycling between high and low temperatures in submarine hydrothermal vents, which can exhibit temperature variations of up to 600K, as well as impact conditions involving temperatures of 1000's of K and pressures of 10's of GPa. However, determining the specific temperatures and pressures or thermodynamic paths that might favor oligoglycine synthesis through laboratory experiments alone can be slow and expensive.

In this work, we use a high-throughput quantum simulation approach to study glycine condensation chemistry under a wide variety of thermodynamic conditions. Using a force-matched semi-empirical quantum simulation method in development in our group, we have determined the free energy surface for aqueous glycine condensation reactions from moderate to extreme temperatures similar to oceanic hydrothermal vents (1g/cm³ and temperatures ranging from 300 K to 1000 K). We predict that temperatures at 400 K and below glycine favor dipeptide formation whereas higher temperatures facilitate the reverse hydrolysis reaction, which is correlated with a shift in the location and characteristics of specific reaction bottlenecks or barriers. In addition, we have studied impacts of aqueous proteinogenic amino acids at conditions reaching 48 GPa and 3000 K. Here, we probe a relatively unstudied mechanism for prebiotic synthesis where sudden heating and pressurization causes condensation of complex carbon-rich structures from mixtures of glycine. These carbon-containing clusters are stable on short timescales and undergo a fundamental structural transition upon expansion and cooling to form sp²-bonded structures include large nitrogen containing polycyclic aromatic hydrocarbons (NPAHs) with a number of different functional groups and embedded bonded regions akin to oligo-peptides. Our results highlight the significance of both the thermodynamic path and local chemical self-assembly in forming prebiotic species during shock synthesis. This can help guide future experimentation by providing both a possible synthetic mechanism as well as a catalogue of possible chemical products to be investigated.

Rotational Spectroscopy Meets Quantum Chemistry for Elucidating Astrochemical Challenges

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Cosmic evolution is the tale of progressive transition from simplicity to complexity. The newborn universe starts with the simplest atoms formed after the Big Bang and proceeds toward astronomical ‘complex organic molecules’ (COMs). Understanding the chemical evolution of the universe is one of the main aims of Astrochemistry, with the starting point being the knowledge whether a molecule is present in the astronomical environment under consideration and, if so, its abundance. In this context, molecular spectroscopy plays the central role: because of the tremendous distances involved, there is no chance to do direct experiments on astrochemical processes, and detection via interaction of molecules with radiation is the only viable route of investigation. The astronomical observation of the spectroscopic features of a given molecule is the definitive, unequivocal proof of its presence in the astronomical environment under consideration, with the overwhelming majority of gas-phase chemical species being discovered via their rotational signatures [1-3]. However, the interpretation of astronomical detections and the identification of molecules are not all straightforward.

Among the goals of astrochemistry, the detection of prebiotic COMs in astrophysical environments, and in particular in star forming regions, is fundamental in view of possibly understanding the origin of life. While, nowadays, the evidence for molecular complexity in the universe is undisputed, there is still much to be understood about what prebiotic molecules are present and how they are formed in the typically cold and (largely) collision free environment of the interstellar medium. By means of selected examples [4-7], it will be shown that: (i) state-of-the-art computational approaches are required to derive structures, energies, spectroscopic properties, and thermochemical data for an accurate characterization of the prebiotic COMs under consideration and their potential precursors [3,8]; (ii) crucial challenges in astrochemistry can be successfully overcome by combining state-of-the-art computational spectroscopy approaches [9] with experiment in the field of rotational spectroscopy.

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Interplay Between Experiment and Computer Simulation to Elucidate the Amide Bond Formation at Silica Surfaces in a Prebiotic Context

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A possible fate of glycine, as well as of the other aminoacids, is to reach Earth through meteorites or comets to become one of the building blocks for the formation of the pristine polypeptides [1]. This step is, indeed, very difficult, as even the condensation reaction between two aminoacids is thermodynamically disfavored in water with high kinetic barriers. The role of mineral surfaces in promoting the formation of peptides in the prebiotic era by condensation reaction of aminoacids has long been established [2]. We contributed to the field through experiment and simulation [3], focusing on common oxides, as potential helpers in the formation of small glycine oligopeptides. Here, we propose the mechanism of the amide bond formation between non-activated carboxylic acids and amines (simpler analogous of aminoacids), hosted at the surface of amorphous silica. We elucidate the mechanism by a combined use of molecular simulation through quantum mechanical calculations based on density functional theory (B3LYP-D3/6-311++G(d,p)) and experimental infrared spectroscopic measurements. Experiments based on infrared spectroscopy carried out on carefully thermal treated silica samples, identified very weakly interacting SiOH surface group pairs, as key sites for hosting and activating, ionic and neutral pairs of the reactants, whose simultaneous presence is crucial for the amide bond formation. The atomistic view provided by DFT modelling revealed the catalytic site envisaging pairs of surface silanol (Si-OH) groups ca. 5 Å apart (Fig. 1). We clearly showed that the removal of one Si-OH group brings the reactant in a fully ionic state, *de facto* hindering the amide bond formation. The proposed mechanism on dry silica resembles that operative in the ribosome for the peptide bond formation [4], in which the Si-OH groups at silica play the role of water in the biological system.

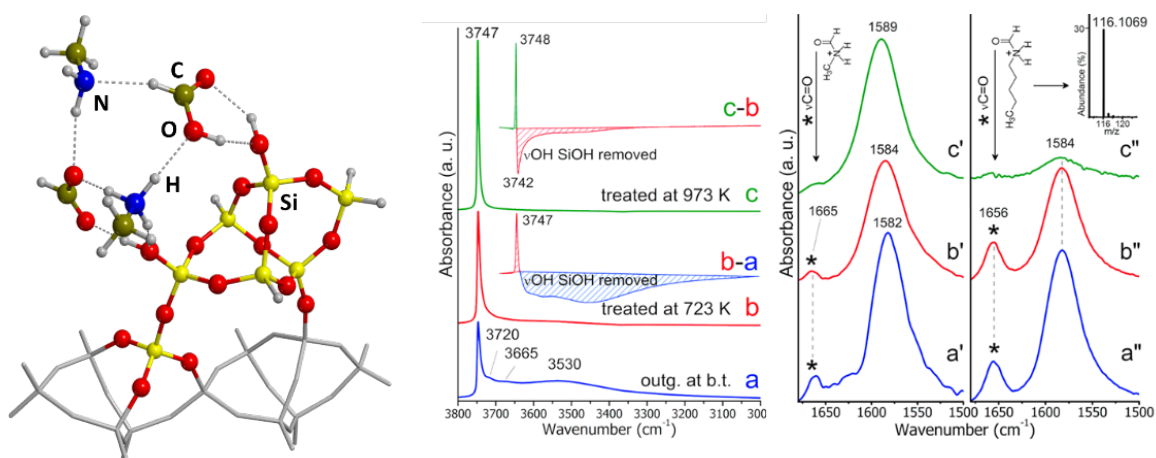


Figure 1. Left: QM model of the silica active site interacting with the neutral/ionic pairs. IR spectra of the silica sample in the OH and C=O stretching regions.

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3D Presentation Rosetta-Philae – The Detection of Organic Molecules on the Surface of a Cometary Nucleus

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ESA's Rosetta mission had made spectators from all over the world dream: On Wednesday, 12 November 2014, the Rosetta mission tried to pose the little robot Philae on the nucleus of comet 67P/Churyumov-Gerasimenko. The Rosetta Space Probe aimed to collect information about the composition of the comet nucleus during its spectacular approach to the sun [1]. Rosetta is the first probe to place itself in orbit around the comet and to place a lander on the surface of a cometary nucleus. The Rosetta probe carried 11 scientific instruments and a Philae lander which itself comprises 10 additional instruments. After 10 years of travel, the separation of the Philae lander from the Rosetta orbiter was carried out on November 12, 2014. The cometary sampling and composition (COSAC) instrument, a device onboard Philae, which we developed in an international partnership lead by the Max Planck Institute for Solar System Research, is a gas chromatograph using eight stationary phases coupled with a mass spectrometer time of flight type. 25 minutes after Philae's landing and bouncing on the cometary nucleus, COSAC successfully performed the first chemical analysis of cometary surface material that cannot be analyzed from the Earth. 16 organic molecules were identified in the cometary sample by using COSAC's MS-only mode [2]. After two additional bouncing events Philae finally landed on the cometary surface and operated for 60 h. During this time the COSAC instrument recorded 420 mass spectra in the enantioselective GC-MS mode. The identification of organic species in these mass spectra remains difficult because of the unexpected 'vertical' landing of Philae and the unexpected low amount of sample that was filled into the oven of COSAC's sample injector system. The first results of the analysis of the cometary nucleus surface by the COSAC instrument will be presented. These *in situ* cometary results will be interpreted in relation to laboratory experiments that allow for the simulation of cometary ices by condensing volatile molecules such as H₂O, NH₃, CO, CO₂, and CH₃OH in an ultra-high vacuum from the gas phase onto a cooled surface of $T = 12$ K. The room temperature residues of the cometary ice analogues were shown to contain amino acids [3], aldehydes [4] and ribose [5] as produced in form of simulated cometary ices in the laboratory [6]. The laboratory simulation experiments thereby confirm data on the chemical composition obtained by the Rosetta-Philae cometary probe.

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The Role of Sulfur and Chemical Selection at the Origins of Life

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A central problem for the prebiotic synthesis of biological amino acids and nucleotides is to avoid the concomitant synthesis of undesired by-products. In this talk selectively accumulated and purified glycolaldehyde and glyceraldehyde as stable crystalline amins will be discussed, which permits selective ribonucleotide synthesis, even from complex sugar mixtures. Amino formation also overcomes the thermodynamically favoured isomerization of glyceraldehyde into dihydroxyacetone and provides a novel pathway to amino acids that avoids the synthesis of the non-proteinogenic α,α -disubstituted analogues [1].

The essential role of sulfur in the citric acid cycle, non-ribosomal peptide synthesis and polyketide biosynthesis point towards thioester-dependent peptide ligations preceding RNA-dependent protein synthesis during the evolution of life. However, a robust mechanism for aminoacyl thioester formation has never been demonstrated. Here a chemoselective, high-yielding α -aminonitrile ligation that exploits only prebiotically plausible molecules to yield α -peptides in water will be presented [2].

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Photochemical synthesis, chirality and detection of the building blocks of life in ‘simulated’ cometary matter

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Introduction: The original appearance of chiral organic molecules in our universe is an essential component of the asymmetric evolution of life on Earth. Simulated interstellar ice experiments have indicated that circularly polarised light could be the initial source of life’s handedness following prebiotic astrochemical condensation of primordial gases (Meinert et al. 2011). With advanced analytical techniques, chiral sugar molecules (Meinert et al. 2016, Nuevo et al. 2018), amino acids (Munoz Caro et al. 2002, Meinert et al. 2012) and/or their molecular precursors produced within these interstellar analogue ices have been detected and are likely to be abundant in interstellar media. These molecular species are considered key prebiotic intermediates in the first steps towards the formation of biomolecular homochirality.

The study of interstellar ices (H₂O, CO, CO₂, CH₃OH, NH₃, CH₄, etc.) – widely observed in the mid-infrared range around protostellar objects (Öberg et al. (2011)), from which planets, but also debris such as comets and asteroids form – provides key information about the pristine materials present in the early solar system and clues for how solar system dynamics/processing could have redistributed and amplified any initial chiral bias among various solar system bodies.

Interstellar Analogue Ices: Laboratory experiments simulating the energetic (e.g. UV photons and cosmic rays) and thermal evolution of interstellar ices will be reported, summarizing recent detections on amino acids, aldehydes and sugar molecules. Moreover, our team proposes a versatile pathway toward the abiotic synthesis of phosphorus (III) and (V) compounds (**Fig. 1**) in phosphine (PH₃) doped interstellar analogue ices upon interaction with ionizing energy (Turner et al. 2018). Phosphorus signifies an essential element in molecular biology, yet the underlying synthetic routes to phosphorus-bearing biomolecules along with their precursors are still in their infancy. We recently succeeded in generating phosphorous oxoacids (Turner et al. 2018) as well as alkylphosphonic acids (Turner et al., *unpublished*) in PH₃-doped ices. This discovery opens a previously overlooked formation route of organo-phosphorous compounds in extraterrestrial ices. The significance of our results arises since these ices are considered as analogues of pre-cometary and/or the soluble part of meteoritic organic matter, although a precise astrophysical scenario is still debated.

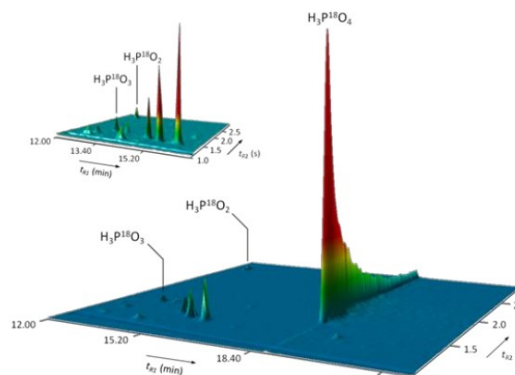


Fig. 1: Phosphorus oxoacids formed in a bimolecular ice system (H₂¹⁸O–PH₃), Turner *et al.* (2018).

When did life started to favor one of its mirror-image twins? Based on *in-situ* observations and laboratory studies, we propose that the selection of contemporary biomolecular handedness occurred when chiral biomolecules were synthesized asymmetrically through interaction with circularly polarized light (cpl) in interstellar space (Meinert et al. 2011). Due to a true chiral influence of cpl (Barron, 1994) the interaction with racemic or achiral molecules generates enantiomerically enriched mixtures. Previous experimental results on the asymmetric photolysis of amino acids (Meinert et al. 2014), as well as the absolute asymmetric synthesis from achiral interstellar ice precursor molecules (de Marcellus et al. 2011), revealed polarization- and energy-controlled induced enantiomeric enrichments. We will therefore highlight significant results on our on-going cometary ice simulation experiments, the chiroptical properties of newly targeted sugar molecules in the UV and present future strategies towards furthering understanding the origin of asymmetric prebiotic molecules.

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Thermophoresis and the “Origin-of-Life” concept

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Formamide is of special interest in the 'origin-of-life' concept, because it was shown to form a number of prebiotic molecules under catalytic conditions and at sufficiently high concentrations [1]. For nucleotides and short DNA strands, numerical finite-element calculations have shown that a high degree of accumulation in hydrothermal pores occurs [2]. Using thermophoretic data of the formamide/water system measured with Infra-Red Thermal Diffusion Forced Rayleigh Scattering (IR-TDFRS) we show that the same combination of thermophoresis and convection in hydrothermal pores leads to accumulation of formamide up to concentrations high enough to initiate synthesis of prebiotic nucleobases. The high degree of formamide accumulation is due to an unusual temperature and concentration dependence of the thermophoretic behaviour of formamide. Starting with a formamide concentration of 10-3 wt%, estimated to be typical in shallow lakes on early earth, the accumulation-fold in part of the pores increases strongly with increasing aspect ratio of the pores, and saturates to highly concentrated aqueous formamide solutions of approximately 85 wt% at large aspect ratios [3]. Time dependent studies show that these high concentrations are reached after 45-90 days. Further, we derived a heuristic model to illuminate the accumulation process and understand the dependence of the accumulation on pore geometry [4].

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On the formation of complex organic molecules from gas phase ion chemistry: simulations and experiments

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Ion-molecule reaction can be taken in consideration to understand how can be synthesized complex organic molecules in space [1]. In the present contribution, we focus on potentially prebiotic molecules, like formamide, urea or glycine. This work was conducted coupling, when possible, atomistic simulations, observations and laboratory experiments.

From computational point of view, direct dynamics simulations were used, from which it was shown that some reactions are good candidates as synthetic routes [2].

In some cases, we have found that different isomers were obtained, in particular for urea [3] and glycine [4].

Experimentally, ion-molecule reactions were conducted in a modified Paul ion trap at CLIO facility (Centre Laser Infrarouge d'Orsay) in Orsay [5], where the structures were probed by IRMPD (IR multiple photon dissociation) spectroscopy in the 2,5-10 μm region using an OPO/OPA laser and a free electron laser. Interestingly, we noticed that glycine can be formed by IR assisted reaction starting from a stabilized ion-molecule complexes.

Atomistic simulations were also useful to rationalize these experiments.

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A computable Ariadne's thread from 1-C compounds to RNA

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Life is made of the intimate interaction of metabolism and genetics, both built around the chemistry of the most common elements of the Universe (hydrogen, oxygen, nitrogen, and carbon). The transmissible interaction of metabolic and genetic cycles results in hypercycles of organization and deorganization of chemical information, of living and non-living. The origin-of-life quest has long been split in several attitudes exemplified by the aphorisms “genetics-first” or “metabolism-first”.

Overstepping the opposition between these approaches by a unitary theoretical and experimental frame, and taking into account energetic, evolutionary, proto-metabolic and ur-environmental aspects, we propose a simple pathway leading to a complete prebiotic reactive system. Specifically, we analyze the synthetic reactions leading from the one-carbon atom compounds HCN and its hydrolyzed form NH_2COH formamide to prebiotically relevant compounds in the presence of catalysts.

We observe the formation of all the extant biological nucleic bases, of carboxylic acids, of aminoacids and of condensing agents in the presence of tens of catalysts of terrestrial origin and of 12 meteorites.

We also observe in the same chemical frame the formation of cyclic nucleotides and their spontaneous polymerization to oligonucleotides, their terminal ligation yielding longer polymers, a ribozyme activity causing the terminal transfer of nucleotides between in vitro abiotically generated oligomers. In vitro generated oligonucleotides thus automatically increase the chemical information of the system. This is not to say that from a formamide test-tube one can magically obtain RNA. Numerous hurdles remain and the results are so far very partial. Anyhow: (i) all extant nucleic bases can be abiotically synthesized. (ii) Nucleosides: the formation of adenosine, thymidine, cytidine, and uridine under proton irradiation is observed. (iii) Phosphorylation: cyclic nucleotides form from preformed nucleosides. (iv) Polymerization: the process has been characterized for 3',5'-cGMP, 3',5'-cAMP, and 3',5'-cCMP. These results entail that the spontaneous generation of proto-metabolic and proto-genetic systems would have required a not exceedingly complex initial set-up. Rather, it was probably the result of the interplay between combinatorial chance and thermodynamic necessity of the existing most abundant atoms.

Structural and energetic compatibility: the driving principles of molecular evolution

Judit E. Šponer, Jiří Šponer, and Ernesto Di Mauro

Astrobiology 2019

A Universal Geochemical Scenario for Formamide Condensation and Prebiotic Chemistry

Raffaele Saladino, Ernesto Di Mauro, and Juan Manuel Garcia-Ruiz

Chemistry 2019

Stabilization of short oligonucleotides in the prebiotic mix: the potential role of amino alcohols

Samanta Pino, Ernesto Di Mauro, Giovanna Costanzo, Raffaele Saladino, Ondrej Šedo, Zbyněk Zdráhal, Jiří Šponer, Judit E. Šponer

ChemSystChem 2019

Surface Chemistry and the Origins of Life

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The implication of mineral surfaces in the origins of life has been proposed as far back as 1951, in a book by Bernal. Since that date, the attention of the OOL community has periodically been drawn back to surfaces by such developments as

- The experimental demonstration by Lahav and Fripiat that amino acids can be polymerized to peptides on clay minerals, through the use of wetting-and-drying cycles, followed by the studies of Ferris et al. on nucleotides polymerization to small RNAs
- The elaborate scenarios devised by Wächtershäuser on the establishment of surface metabolism on metal sulfide surfaces (the “sulfur world”), and the reflexions by Russell et al. on hydrothermal vents chemistry
- The provocative ideas of Cairns-Smith on clays as the first living systems and the “genetic takeover”

Experimental testing of these hypotheses requires studying the interactions of small molecules with mineral surfaces and their reactivity in that environment. These topics have long been studied by surface scientists working in fields such as heterogeneous catalysis or surface functionalization. Only recently have a few of these teams become interested in OOL studies, helping to verify, understand and develop earlier intuitions and serendipitous discoveries.

This contribution will briefly outline some aspects of surface science that are relevant for prebiotic chemistry reactions:

I. Adsorption

Adsorption mechanisms have long been studied by geochemists, electrochemists and colloid chemists. They can be described at the macroscopic level and rationalized by physical chemistry models. Different adsorption mechanisms are more or less energetic, and may induce the selection of some molecules from complex mixtures (adsorption selectivity).

II. Surface characterization

Several characterization tools (LEED, STM...) are uniquely suited to molecules adsorbed on model crystalline surfaces, typically metallic single crystals in high vacuum. Other techniques extend to less regular flat surfaces, including under aqueous solutions (IRRAS, QCM, AFM...) and are therefore suited to exploring early earth scenarios. For divided matter (nanoparticles), vibrational (IR, Raman) and NMR can be applied in situ to adsorbed molecules and their transformation products.

III. Catalysis by surfaces

When dealing with reactions on surfaces, it is fundamental to disentangle thermodynamic from kinetic (catalytic) effects. From the thermodynamic point of view, surfaces may act as platforms allowing to capture free energy from macroscopic imbalances. From the catalytic point of view, surface sites may very selectively open some reaction channels by activation of adsorbed biomolecules and may have played the role of current enzymes in “ancestors” of metabolic pathways – this is the hypothesis of geochemical continuity. The similarities between some primordial mineral phases and catalysts used in the chemical industry opens the way to fruitful transfer of concepts to the OOL studies.

From ancient to modern RNA worlds and vice versa

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A crucial point in early life history is to understand how evolution passed from complex prebiotic chemistry to simple biology. Current cellular facts allow us to follow the link from chemical to biochemical metabolites, mainly metallic-cluster compounds and ribonucleotidic cofactors. In this context, the “RNA world” hypothesis proposes that early in the evolution of life, ribozymes were responsible for the storage and transfer of genetic information and for the catalysis of biochemical reactions. Accordingly, the hammerhead ribozyme (HHR), the hairpin ribozyme, and the ribozyme contained in hepatitis- δ virus (HDV) belong to a family of endonucleolytic RNAs performing self-cleavage that might occur during replication. Furthermore, regarding the ultraconserved occurrence of HHR in several genomes of modern organisms (from mammals to small viroids) these small ribozyme motifs have been regarded as vestiges of a pre-RNA world. The existence of contemporary life in extreme conditions, providing habitats for cellular and viral species, encourages us to focus on the activity, persistence and dynamics of small RNAs under such conditions. All the results exemplify ubiquitous features of life, notably the plasticity and efficiency of small RNAs, as well as their diversity and adaptability to various extreme conditions, traits that must have originated in early life history to generate novel RNA populations. In this talk we will present some arguments supporting such an ancient world, as well as our experimental results in this frame.

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Ribonucleotides and the RNA World

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How the ubiquitous nucleic acid-based genetic system of extant life may have originated from the prebiotic soup one of the major unsolved problems in contemporary biology. The accidental discovery of catalytic RNA molecules, i.e., ribozymes, that behave like proteins catalyzing biochemical reactions, has provided considerable credibility to prior suggestions that the first living entities were largely based on ribozymes, in an early stage called the RNA world. Although at the time being the hiatus between the primitive soup and the RNA world is discouragingly enormous, the catalytic, regulatory & structural properties of RNA molecules, combined with their ubiquity in cellular processes, are consistent with the proposal that they played a key role in early evolution and perhaps in the origin of life. There are many definitions of the RNA World, including several contradictory ones. One could say that it is an early, perhaps primordial, stage during which RNA molecules played a much more conspicuous role in heredity and metabolism. The same is probably true of ribonucleotides, which exhibit an extraordinary plasticity, as shown by their manifold biochemical roles, as energy-carrying compounds, precursors of deoxyribonucleotides, as well as precursors of coenzymes, histidine, alarmones of some antibiotics.