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Interaction of thymine and uracil with nickel and cadmium hexacyanoferrates (II) and its implication in chemical evolution and the origin of life

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Abstract

Nickel and cobalt hexacyanoferrates (II) complexes were synthesized and characterized by elemental and spectral studies. Adsorptive interaction of nucleic acid bases (thymine and uracil) on nickel and cobalt ferrocyanides were studied at pH range 1.0 – 10.0 and a temperature of 30 ± 1^{o}c. Maximum adsorption of thymine and uracil was found to occur at neutral pH on both adsorbents. The adsorption of thymine and uracil follow the order NiFc > CdFc. The Langmuir type of adsorption model was followed in concentration range 10^{-4} -10^{-5} M of thymine and uracil solutions. Results on the present studies suggest the importance of metal ferrocyanides as a possible condensing agent for bio-molecules during the course of chemical evolution and origins of life on Primitive Earth.

1. Introduction

Due to easy of formation of cyanide under prebiotic conditions, cyanide ion might have formed stable complexes with transition metal ions present on primitive Earth. It is well established that metal ferrocyanides acts as adsorbents [1], ion-exchangers [2] and photosensitizers [3, 4]. A search of literature indicated that few reports available on interaction of amino acids with metal ferrocyanides [5], but no report available interaction of nucleic acid bases with metal ferrocyanides. In view of this attempt was made to study adsorptive interaction of nucleic acid bases with metal ferrocyanides. In addition present work described interaction of thymine and uracil with nickel and cobalt ferrocyanides and their implications in chemical evolution.

2. An Experimental Section

All chemicals used were of AnalaR grade. Nickel and cadmium ferrocyanides were prepared by method reported in literature by Kourim [6]. Both metal ferrocyanides were characterized by elemental and spectral studies. Percentage composition of elements in metal ferrocyanides is given in Table 1. Infrared spectra of the nickel and cadmium ferrocyanides were recorded in KBr disc, on Beckman IR-20 spectrophotometer. Both metal ferrocyanides shows a broad peak at 3600-2625 cm^{-1} is characteristic of water molecule and OH group. Also a peak at around 1590-1623 cm^{-1} is due to H-O-H bending. A sharp band 2000 cm^{-1} and a broad peak at 590-595 cm^{-1} were observed in both metal ferrocyanides, is characteristic of cyanide and Fe-C stretching, respectively. The absorbance of thymine and uracil were measured spectro-photometrically at their corresponding λ_{max} 265.5 nm and 258.5 nm, respectively. The amount thymine and uracil absorbed were calculated by the difference in their concentration before and after adsorption.

3. Results and Discussion

Percentage uptake of thymine and uracil on metal ferrocyanides was calculated. Adsorption process follows Langmuir model equation in general. The maximum uptake of thymine and uracil on metal ferrocyanides follow the order Ni Fc > Cd Fc.

4. Equations

Sorption data have been correlated with Langmuir adsorption model [7] given by

$$\frac{1}{q_{eq}} = \left(\frac{1}{Q_o}\right) + \left(\frac{1}{C_{eq}} \quad \frac{1}{b}\, Q_o\right)$$

where, C_{eq} is equilibrium concentration of thymine and uracil, b is the constant related to equilibrium constant or bonding energy (b α $e^{-\Delta H/RT}$), the parameter b reflects the steepness of the approach to saturation, more precisely, the b value is the reciprocal of concentration at which half saturation of the adsorbent is attached). Q_{eq} is the amount (mg) of adsorbate adsorbed per gram of adsorbent, and Q_o is adsorption maxima, i.e. mg of thymine and uracil required per gram of metal ferrocyanides for forming a complete monolayer on the surface.

5. Summary and Conclusions

Present study reveal that metal ferrocyanides present at the shore of primeval seas could have interacted with thymine and uracil in such a way as to concentrate them from the dilute prebiotic soup during the course of chemical evolution. Biomonomers, thus concentrated, are thought to have been protected from degradation and undergoes a class of reactions of prebiotic relevance producing biopolymers essential for the formation of the first living cell in this planet.

Acknowledgements

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Aqueous alteration and putative microbial mediation in NIPR L chondrites

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Abstract

This work emphasizes aqueous and putative microbial mediation of NPR L chondrites. The microbial mediation is studied by optical microscopy (biogenic minerals, textures, morphology) and by FTIR-ATR spectroscopy (organic material, composition of fine-grained altered part: serpentine, iron oxides, amphibole).

1. Introduction

Chondrite constituents are considered as solar cloud condensates and surviving primordial dust grains accumulated in chondrules and minerals. The chondrites are fragments of asteroidal sized parent bodies where several transformation processes occurred: thermal metamorphosis, impact induced shock transformations and aqueous alteration. The aim was a high resolution textural and mineralogical characterization of the transformation products of UOC. The first overview of petrographical studiers of NIPR Collection L series have been made by [1], [2]. The shock metamorphic features (planar fractures, mosaicism) observed in all of studied samples [3].

2. Samples and methods.

Four Antarctic L chondrite thin section (30 μm) were studied: Y74191 (L3), Y74355 (L4), Y79057 (L5) ALH769 (L6).

High resolution petrographic structural, textural studies were undertaken on four thin sections using a petrographic microscope (OM). We used FTIR-ATR spectroscopy (Bruker Vertex70 device attached Hyperion2000 microscope, detection between 600-4000 cm^{-1}) for the determination and distribution of micro-mineralogy and organic compounds.

3. Petrography

Yamato-74191 (L3) chondrite: The sample has a fine-grained groundmass and the chondrules have sharp rims. The inhomogeneity in pyroxenes of the measured samples are well observed. The thin section consists of 45% olivine and 55% pyroxene phenocrysts. The chondrules are generally about 0.8 mm in diameter, but larger chondrules with diameter between 1 and 1.5 mm, and smaller ones with diameter between 0.1-0.3 mm can also be observed.

Yamato-74355 (L4) chondrite: The Yamato-74355 consists of well-formed round-shaped chondrules (60%), chondrule fragments (10%) and fine-grained groundmass (20%) with olivine and pyroxene phenocrysts (10%) of about 0.03 and 0.12 mm in diameter. (The abundance ratio for phenocrysts is 55% olivine and 45% pyroxene.) The average diameter of chondrules is 0.1-2 mm. There are opaque patches consisting of troilite and metallic iron and having diameter between minimum 0.4-0.7 mm and maximum 2-3 mm.

Y-790957 (L5) chondrite is a strongly brecciated chondrite with a small number of chondrules but large number of mineral fragments having 0.03-0.1 mm size on average. The whole sample has porphyritic texture.

Allan Hills-769 (L6) chondrite: The sample consists of chondrules, crystals, chondrule fragments and recrystallized groundmass. The size of chondrules and chondrule fragments varies between 1.2 – 3 mm.

4. Putative microbial features

Mineralized microbially produced texture (MMPT) in the form of pearl necklace-like, vermiform inner signatures, embedded in the stone meteorites has been observed for the first time. Our observations (OM) focused on the iron-containing opaque grains, glass, olivines and pyroxenes, which were well populated by micrometer-sized microbial filamentous elements and clusters in their boundary region within the matrix and inside the minerals. In the chondritic textures we observed that microbial “invasion” started in the fine-grained matrix and extended into the chondrules mainly through the Fe-containing minerals. The MMPT is very extensive, reaches 70-80 % of the sections, and is intimately woven in the full cross-section of the thin sections of the whole stone meteorite. All thin sections showed signs of Fe mobilization and oxidation (reddish-brown haloes around mineral grains, reddish-brown filaments) (Fig. 1).

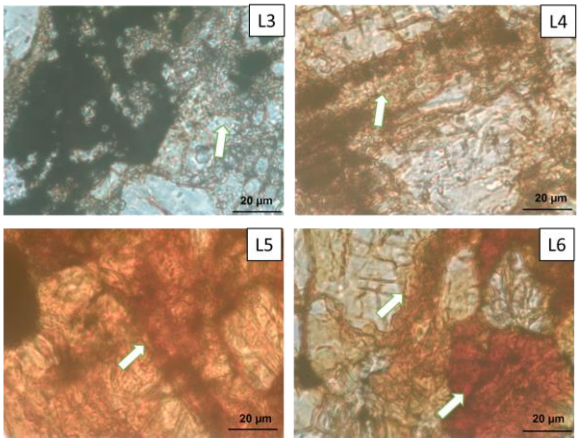

Fig. 1: Putative microbial mediation in NIPR L series (shown by arrows) – necklace-like filamentous FeOB

5. FTIR-ATR

The iron-oxidizing microbial structures have a mixed composition containing iron oxides (ferrihydrite, goethite, hematite) [4] with serpentine [5], in host minerals olivine [5], and pyroxenes (diopside, enstatite) [5], and opaque minerals (troilite, chromite) [5] (Table 1). Hydrocarbon compounds were also detected (long chain hydrocarbon, diene; and C-H stretching of aliphatic hydrocarbons [6]. The presence of olivine and serpentine spectra proves the weathering of olivine, while the appearance of ferrihydrite and hematite corresponds to bacterial originated remobilization of iron from olivine and troilite (Fig. 1). IR vibrations of isoprenoids were also detected [6]. Moreover in weathered part of chondrules hornblende [5] was detected, which indicates aqueous alteration. This phase was firstly described in Tieschitz meteorite [7]. The microbial mediation was observed in other L chondrites from Hungary [8]

Summary and Conclusions

Our data confirm dense and invasive microbially mediated contamination in the chodrites, supported by microtexture, micromineralogy and embedded organic compounds, which effected most of the mass of the samples. As the transformation processes are supposed to happen on the parent bodies, it raises contradictions concerning a possible terrestrial contamination as it seems that these products manifest in microbially mediated texture. In our study we offer basically different interpretation to solve these contradictions.

Table 1: Biogenic minerals and organic compounds of studied NIPR L series: The occurrence of minerals and organic compounds can be seen in columns.

	No. spectra	42	21	25	**22**
Mineral phase	**References**	**NIPR L3**	**NIPR L4**	**NIPR L5**	**NIPR L6**
olivine	5	20	14	11	8
serpentine	5	7	4	6	11
enstatite	5	3	2	2	2
diopside	5	4	1	0	1
feldspar	5	0	0	1	0
hornblende	5	0	0	3	1
ferrihydrite	4	5	0	0	0
troilite	5	9	4	2	4
chromite	5	0	0	1	0
hematite	4	0	0	0	0
goethite	4	2	0	5	0
Organic compounds		0	0	0	0
v C=C/C-O	6	7	0	0	0
vs CO	6	7	0	0	0
d CH2	6	37	18	4	6
C-N, CH deformation	6	40	0	0	2
C-N N-H amide II	6	40	18	16	10
C=C asym. Stretch	6	0	0	0	0
amide I C=O, C-N, N_H	6	40	18	16	4
v as COOH	6	0	0	0	0
C-O	6	0	0	0	0
CO	6	42	21	21	18
CO	6	42	21	21	18
C-H sym. Stretch CH2	6	42	17	21	8
C-H asym. Stretch CH2	6	42	17	17	8
CH2 /C=C	6	0	0	4	0
OH	6	8	12	8	4

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Astrobiological interest of deep subsurface geomicrobiology

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Abstract

If we want to detect signs of life on Mars, either extant or extinct, drilling missions to gain access to the subsurface are indispensable since life on the surface is virtually impossible due to the extreme doses of UV radiation, lack of liquid water, low temperatures and high oxidant conditions. But selecting the appropriate technologies for life-sign detection in the subsurface poses an important challenge since current knowledge of the dark biosphere is still very scarce.

Introduction

Economic and technical constraints have limited the amount of information obtained from devoted geomicrobiological drilling studies. Most of the continental subsurface data has been obtained using pre-exisiting subterranean "windows" (artesian wells, springs, deep mines, underground locations for waste disposal and underground research facilities) all of them with important limitations.

The picture that is emerging from the available data shows a variable number of cells in the subsurface, probably related to the geology and hydrology of each studied system. In general, the number and diversity of microorganisms decreases with depth and Bacteria outnumber Archaea. Within Bacteria the most common detected phyla correspond to Proteobacteria, Actinobacteria, Bacteroidetes and Firmicutes. Within the Archaea, methanogens are recurrently detected in most analyzed subsurfaces together with sulfate reducing activities.

In the study of subsurface environments, one of the most controversial topics is whether the available energy source is endogenous or partially dependent on products generated in the surface. However H2, which can be generated abiotically, seems to be among the most widely used electron donors, although other lithotrophic metabolisms that make use of reduced iron, sulfur and nitrogen have also been detected in the subsurface. More information at a better depth resolution will build up the repertoire of subsurface electron acceptors and donors biologically available in the deep subsurface. Several studies reported the presence of viruses in subterranean environments, but only a more systematic evaluation can accurately assess their role in horizontal gene transfer among microbial populations. Similarly, a thorough analysis is needed to verify the reported presence of fungi as members of the dark biosphere.

Even though drilling and contamination control methodologies are well established, procedures for taxonomic, functional and metabolic analysis are rather diverse and reflect the rapid evolution of this field of study. In any case, the use of complementary techniques is strongly advisable because it helps sort out the most important elements in the system. Of the many techniques used for sample analysis, those based on fluorescence in situ hybridization are of particular interest because they allow a resolution at the micro-niche scale, which cannot be obtained by most of the other currently available methodologies due to the large volumes of sample they require, consequence of the low cell numbers existing in deep low porous rocks.

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M Dwarfs, Super Earths and photosynthetic bacteria: a mix for laboratory studies

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The answer to one fundamental question of mankind, *Are we alone?*, is today closer than ever. The possibility to achieve this goal, is in fact supported by the fast developing in the highly interdisciplinary field of study of extrasolar planets. The observational data on extrasolar planets (more than 3500 discovered so far) show such striking properties (e.g. [9]) as well as the complexity of planet formation and evolution processes, that we are just starting to realize. Furthermore, a lot of new discoveries concern planets with Earth or pretty larger than Earth size (the so called Super Earths) close or inside the Habitable Zone (HZ, [6]) of their host star. Habitable planets are likely to exist not only around stars similar to the Sun, if current theories about terrestrial climate evolution are correct, but also around cooler stars like the M Dwarfs ones ([8]). For this reason, great observational efforts are ongoing, culminating today in the promising candidate in orbit of our closest star, Proxima Centauri ([1]), and the first habitable system, Trappist-1 ([5]), hosting at least two habitable planets out of seven rocky planets orbiting a small and very cool star (M8 spectral type). The distribution of extrasolar planets, discovered so far, shows a large number of low mass companions around M stars with an occurrence of 40% for stars that host planets with minimum mass between 3 and 30 $M_\oplus$, orbital periods shorter than 50 days ([7]), radii between those of the Earth and Neptune (1–3.8 $R_\oplus$). These high occurrence rates have a consequence: Super Earths represent the most common type of planetary systems in the Galaxy ([7]). Some of these planets O_2-rich atmospheres that lie within the HZ around their parent star are, in all probability, inhabited. The discovery and characterization of Earth-like planets with the eventual search for life is, arguably, one of the most exciting scientific endeavors of this decade. In this framework, it is critical to determine the types of biosignatures that we should be looking for when designing the next generation of ground- and space-based instruments that will observe these planets at high spectral and possibly spatial resolutions. The search for life signature requires the knowledge of planet atmospheres, main objective of future exoplanetary space explorations. Moreover, the recent finding of cyanobacteria able to use infrared light for oxygenic photosynthesis due to the synthesis of chlorophylls d and f, extending in vivo light absorption up to 750 nm respectively ([4]; [2]), suggests the possibility of exotic photosynthesis in planets around M stars. Knowing which pigments cyanobacteria can produce, when exposed to radiation sources expected for planets orbiting around M-dwarf stars, is relevant for future astronomical observations, such as those based on spectrometers mounted on large ground telescopes, like HARPS at ESO's La Silla Observatory, HARPS-N and GIARPS mounted on TNG in La Palma, or the forthcoming ESPRESSO spectrometer at the ESO's Very Large Telescope. Next generation satellites (JWST, ARIEL) are designed to detect exoplanet atmospheres. The proposed ARIEL telescope will observe in the spectral range where gases such as H_2O, CO_2, CH_4 NH_3, HCN, H_2S can be observed. To contribute to the current astrobiology challenges in searching for life elsewhere, our project will then focus on two crucial goals: 1) enhancing our knowledge of habitability, by investigating the adaptability of cyanobacteria to M-star environment with laboratory simulations; 2) mastering the use of spectroscopic remote-sensing of their atmospheric and surface reflectance biosignatures.

At the INAF – Astronomical Observatory, Department of Biology and CNR IFN LUXOR of Padova we are performing laboratory experiments [3] aiming at twofold results. At first we want to understand how photosynthetic biota, once present on an Earth-like planet orbiting in the habitable zone of a star of different spectral type than the sun, can modify its atmosphere. In particular we study how the O_2 – CO_2 balance would differ from the terrestrial one. An ancillary output is to understand if the feature of the "red edge" reflecting property and both the pigment composition and concentration of photosynthetic organisms would be influenced by the extended undergoing to a different radiation spectrum. Studying the different reflectance spectra of the pigments inside organisms grown in different light conditions allows to understand these biophysical properties. In these experiments we analyze the photosynthetic efficiency and gaseous productions of several strain of bacteria with a laboratory set up mimicking the exoplanetary surface temperature and radiation conditions. With this aim we developed a starlight simulator that reproduce the stellar spectrum in the wavelength range (365-940 nm) overlapping the photosynthetic active range (PAR) (280–850 nm).

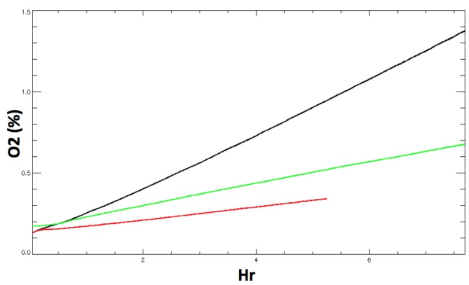

Figure 1: The oxigen production of a cyanobacteria species under simulated solar irradiation (black line) and M7 star simulated irradiation (red line). The green line is the oxigen production of a control organism irradiated with simulated solar light.

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Microbial growth in simulated martian environments

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Abstract

In this study, four new simulants have been developed, and their associated fluid chemistries have been derived for use in a series of microbiological simulation experiments. These experiments will determine if aqueous environments on Mars, past or present, could potentially support microbial life and identify any key geochemical bio-signatures that may arise as a result of that life.

1. Introduction

The widespread presence of hydrated minerals and geomorphological features on Mars suggests water may once have been present on the surface, as result of a hydrological cycle [1-3] producing valley networks and lacustrine environments, or due to long lived impact generated hydrothermal systems [4-5] producing crater lakes. Today, the conditions at the surface are not conducive to sustain liquid water, however, liquid water may exist in the martian subsurface. If so, potentially habitable environments may have existed in the past or exist in the subsurface today, which warrant further investigation. Therefore, we will be conducting a series of simulation experiments that mimic past lacustrine environments and modern subsurface environments. For this the chemical conditions of four key environments will be created, using newly developed simulants and their associated fluid chemistries. These experiments will determine if these environments could support microbial life and identify key bio-signatures that may be produced.

We will present initial results obtained from these simulation experiments. In addition to this, results from thermochemical modelling of these simulated environments will also be presented to show how these environments will develop over geological timescales.

2. Experimental programme

2.1 Simulating the chemical environment

Regolith simulants were developed to reflect varied chemical environments that may have existed over Mars' history, as proposed by [6], and are evidenced by the varied lithologies identified on Mars today. Using published geochemical data to support their design, we have based these new simulants on the following environments: an ancient and unaltered martian bedrock, based on a basaltic shergottite [7]; a contemporary and global regolith chemistry based on Rocknest at Gale crater [8]; a sulfur rich regolith potentially produced under an acidic aqueous environment, based on Paso Robles at Columbia Hill [9]; a haematite (Fe^{3+}) rich regolith that may have formed in an oxidizing and dry environment, based on Haematite slope at Meridiani Planum [10]. The composition of the fluids that could be found on Mars would be representative of the geochemical environment [11]. Therefore, fluid compositions were derived by modelling the water-rock interactions between the simulants and pure water [12]. These fluid chemistries and simulants will then be used in simulation experiments.

2.2 Simulation experiments

Abiotic and biotic experiments will be conducted to identify geochemical changes that may occur as a result of microbial life. Biotic experiments will be inoculated with a microbial enrichment collected from Pyefleet mudflats in the Colne estuary (Essex, UK), rich in sulfur-reducing bacteria and methanogens [13]. These will be added to the simulants and fluids within a benchtop reaction vessel that will simulate the physical conditions found in the martian subsurface. Experiments will mimic a past lacustrine environment at a pressure of 1 bar and temperatures of 10 and 25 °C, to represent a warm, wet Mars as proposed by [3]. Subsurface environments will be simulated using pressures of 1 and 200 bar (equivalent to a depth of 10 m and 2 km, respectively [14]), and temperatures of 5 and 30 °C (representative of depths of 10 m and 2 km, respectively, assuming a surface temperature of 5°C and a thermal gradient of 13 °C km^{-1} [15]). The reaction vessel has a flow-through system, whereby fluid is continuously pumped through the reaction chamber, which is more representative of the open systems that are found on Mars. This system also enables the continuous sampling of the fluid, meaning changing of fluid chemistries can be monitored without altering the water-rock ratio or depressurising the chamber. This offers a significant advantage over traditional batch culture experiments.

Thermochemical modelling using titration and flow though models in CHIM-XPT [16] will determine the resultant fluid chemistries and the secondary minerals formation of these environments, which will help our understanding of how these abiotic and biotic systems might evolve over geological timescales.

3. Implications

The results from these experiments will contribute to our understanding of whether or not the geochemistry and physical conditions found on Mars could support microbial life. It will also identify any geochemical changes that might occur as a result of microbes being introduced to the chemical environment, which could be used as bio-signatures. Any potential bio-signatures identified from these experiments could be targeted by future exploration rovers as indicators for life.

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A hydrothermal-sedimentary origin of life scenario

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Abstract

Prebiotic chemistry leading to the emergence of life could have taken place in volcanic sediments flushed by hydrothermal fluids that were ubiquitous on the early Earth.

1. Introduction

Many locations, ranging from hydrothermal vents, pumice rafts, to continental springs and rivers, have been proposed for the emergence of life on Earth 1-3]. Hydrothermal edifices, in particular, offer a combination of characteristics that make them particularly attractive: concentration of organic molecules in the porous edifices, disequilibrium conditions and protection from harmful UV radiation, presence of transition metal-rich mineral surfaces upon which molecules can con-dense, be structured and complexify [4,5].

2. Results

Using evidence from the oldest, well-preserved volcano-sedimentary rocks (3.5-3.3 Ga), the best available analogues to Hadean sediments, we document from the macrosopic to the microscopic and elemental scale that these porous volcanic sediments (originating from mafic and ultramafic crust) were permeated by hydrothermal fluids at all scales, gently infiltrating between the pores or sometimes more dynamically mixing the volcanic particles (Figure 1 [6, 7]).

3. Discussion

Reduced carbon was brought in by the hydrothermal fluids although carbon of meteoritic origin would also have been relatively abundant, especially in the Hadean era. This UV-protected, subaqueous sedimentary environment, characterised by physical and chemical disequilibria (gradients in temperature, pH, redox and relatively diverse mineral speciation), represented a globally distributed system of miniature chemical reactors in which the production and complexification of prebiotic molecules could have led to the origin of life.

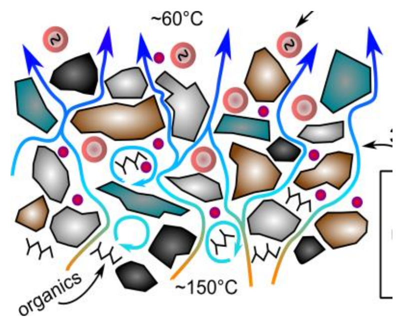

Figure 1. Prebiotic chemistry in hydrothermal volcanic sediments

4. Conclusions

The fundamental importance of these observations is that hydrothermal sediments and these kinds of organic reactions occurring at mineral interfaces must have been ubiquitous on the Ha-dean Earth, and life could have emerged anywhere all over the early Earth – at temperatures (<100°C) conducive to prebiotic chemistry.

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The Role of Atmospheric Nitrogen as a Geo-Biosignature

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Abstract

Nitrogen is an essential element in the building blocks of life and Earth's biosphere. We show that the geobiological nitrogen cycle is a fundamental factor in the Earth's long-time habitability and most likely on Earth-like exoplanets. We discuss the evolution of the Earth's nitrogen atmosphere and its relation with the biosphere. Then we suggest hypothetical atmospheric evolution scenarios: i.) A stagnant-lid regime world where neither plate tectonics nor life evolves, although the Earth like planet has a liquid water ocean on its surface. ii.) An anoxic world where plate tectonics evolves and a liquid water ocean is present on the planet's surface, but no life or only anoxic life forms originated. iii.) An Earth-analogue world with an origin and evolution scenario similar to the Earth. iv.) A world where a terrestrial planet evolved similar to the Earth, but all life forms become extinct. After discussing possible evolution scenarios, we argue that terrestrial planets with nitrogen-dominated atmospheres facilitate an operating plate tectonic regime connected with an enhanced probability of highly developed life forms, whereas the absence of such features most likely implies CO_2-dominated atmospheres.

1. Scientific Relevance

The evolution of an Earth-like planet and its atmosphere is strongly related to the planet's formation process, the host star's activity controlling the escape of a possible hydrogen/helium dominated protoatmosphere, the evolution of the secondary atmosphere, and the planet's impact history including its initial volatile and water inventories [1]. On Earth, about 4.0 billion years ago, a nitrogen dominated atmosphere started to rise during the Archean eon and life as we know it originated. The origin and evolution of life on Earth has been responsible for the modification of atmospheric composition and climate [2]. The biological modulation of the Earth's atmosphere had been extensively discussed [3]. Recent simulations of the atmospheric-biological interaction over geological times on Earth-like planets indicate that the presence of nitrogen and oxygen in combination could be a possible signature of an oxygen-producing biosphere [4]. Although oxygen and ozone are necessary ingredients for the evolution of complex life forms, several theoretical studies have shown that oxygen may also abiotically build up in an exoplanet's atmosphere [5,6]. The possibility of abiotic atmospheric oxygen and ozone in terrestrial exoplanet atmospheres in combination with water implies that such a composition is not necessarily an evidence for a particular planet to be populated by multicellular life forms. One should note that nitrogen is an essential element for life on Earth and it is also involved in limiting nutrients that control autotrophic CO_2 fixation, which in turn is connected to the climate, weathering, and the redox state of Earth's surface over geologic timescales. Our main aim is to investigate how the complex interplay between geophysical factors and life influences atmospheres on terrestrial (exo-)planets. Further we raise the question of which scenarios lead to nitrogen dominated atmospheres on Earth-like planets.

2. Conclusions

We show a strong correlation between a nitrogen dominated atmosphere and water, oxygen and ozone as biosignatures for highly developed life forms on terrestrial planets. The composition of atmospheres originates from complex interactions between the atmosphere, lithosphere and biosphere. Since life forms play an important role in maintaining the nitrogen dominated atmosphere on Earth, if such life and interactions are rare, we expect the atmospheres of most terrestrial planets in the habitable zones to be CO_2-dominated. This molecule presents a number of absorption bands in the infrared, therefore making it detectable from the ground with high-resolution spectrographs attached to the ELTs. Our hypothesis could therefore be proven by characterizing the atmosphere of the Earth-size planets detected by TESS and PLATO.

Acknowledgements

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In-situ detection of biosignatures from 1.9 Ga Gunflint chert with LMS

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Abstract

In this study, we show first data to demonstrate that miniaturized LA-TOF-MS (Laser Ablation – Time of Flight – Mass Spectrometer or LMS) combined with vacuum compatible microscopy system is a powerful tool in investigating the chemical composition of planetary bodies on the micrometer scale. Concerning questions related to the detectability of extinct or extant life, LMS is shown to be sensitive to highlight elemental abundances down to the ppb level and isotopic differences in the per-mil range of accuracy [2], [3]. These constitutes the primary challenge of planetary sciences and astrobiology, specifically, detectability of fossilized microbial colonies possibly preserved on planet Mars [1], [6]. We tested the instrument performance on a chert sample of 1.9 Ga age from the Gunflint Formation. Measurements are performed at infrared, infrared double pulse, visible, and ultraviolet wavelengths of laser irradiation in the fs time domain. We studied *in-situ* the chemical composition of a microfossils colony, different individual fossils, and host minerals. High spatial resolution of our microscope system with an updated procedure of the translation stage calibration allowed us to perform precise ablation of dense fossilized spots on the surface of stromatolite lamination and areas of surrounding Si-rich host.

Introduction

In-situ mass-spectrometry on the surfaces of planetary bodies is a promising technique which is of considerable interest for landed missions and also of particular interest in searches for extinct life on planet Mars. Regarding these question, single grain analysis coupled with sample probing on the macroscale and supported by satellite imaging on the regional level could help to investigate chemical composition of rock units, and gain insights into its formation and evolution [6],[7]. Sensitive elemental and isotopic studies with high lateral and depth resolution are considered to be the critical component for identification of single minerals, e.g. the host minerals of the fossils, and also for identification of putative microscopic fossils, which are usually preserved through permineralization [1], [4].

1. LMS Instrument

The LMS is small instrument suite which has low mass (1500 g), size (length – 120 mm; diameter – 60 mm), low power consumption, robustness in the harsh environments and ability to provide highly accurate measurements. Generally, all these aspects make the development of space instrumentation a challenging endeavour and frequently require lessening of precision of the instrument. In case of LMS, all necessary requirements have been fulfilled during continuous development over more than a decade. In the current state, the laboratory-based version of LMS is small-sized mass-spectrometer coupled with fs-laser ion source which can be switched from the fs-IR to the fs-UV range with an ability to provide two fixed harmonics at any given time (double-pulse). The suite is also coupled with the high vacuum compatible microscope with micrometer resolution. Detailed information about instrument could be found in our previous publications [2], [3], [5], [8].

2. IR and UV ablation studies of Gunflint chert as Martian analogue sample with LMS.

The 1.9 Ga Gunflint chert sample from Schreiber beach, Ontario, Canada, is considered in our study as Martian analogue sample. It was prepared in the form of the thin section and mounted on steel sample holder. Detailed mass-spectrometry studies on dense fossilized spots and clean host areas reveal differences in chemical composition. Main preservation type determined by results of our studies is pyritization of cell walls in mainly chalcedony host.

Fossilized colonies show high C, Mg, S, Fe content where at the same time measurements on pure host contain almost negligible or noticeably lower concentrations of these elements. The laser ablation rate for areas on the host mineral appears to be significantly lower in comparison to the fossils since pure chalcedony is nearly transparent at our IR wavelength. However, successful laser ablation in infrared was achieved by increased laser irradiation.

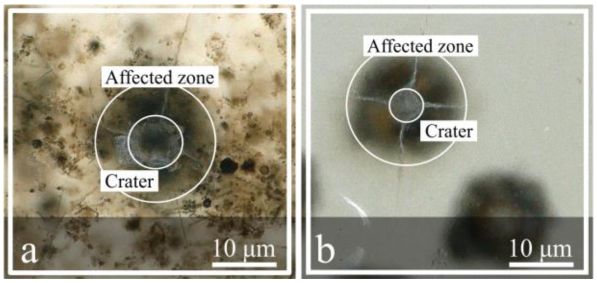

Figure 1: Laser ablation craters on the surface of the Gunflint chert sample obtained on two different areas with IR laser irradiation (equal amount of shots): a) Dense fossilized colony; b) relatively pure host

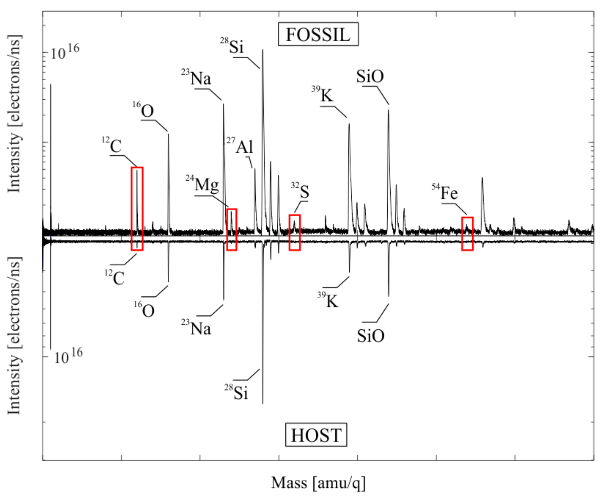

Figure 2: Comparison of two mass spectra from the Gunflint chert sample. The upper part of the plot corresponds to the crater shown in Figure 1a. The lower part of the plot corresponds to the crater shown in Figure 1b.

In comparison with the fs-IR-laser ablation ion source, measurements performed at UV range of laser irradiation offer better detection sensitivity and gentler ablation.

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Towards new potential strategies for biosignatures detection: correlating the physico-chemistry and complexity of amino acids from deep space

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Abstract

Amino acids are high priority targets in the search for life elsewhere in the Universe. However, the wide range of amino acids from abiotic synthesis as revealed from meteoritic findings suggest that amino acids are not unambiguous indicators of life. More fundamental concepts as complexity of molecules are recently being proposed for new strategies for biosignatures detection. Here we present a study, based on quantum chemistry modelling, of the possible link between spectroscopic quantities, a complexity measure, a chirality descriptor and H-bonding network properties for amino acids of the isoleucine series, found in Antarctic meteorites, which are either involved in protein synthesis, featured in human plasma, or external to our biosphere.

1. Introduction

With the observation of liquid water and active geology on the Jupiter's moon Europa and Saturn's moon Enceladus, water ice in the shallow subsurface of Mars, and the expected increase in the number of observed exoplanets, planetary exploration is making fundamental steps in the search for life beyond Earth [1]. However, current strategies for biosignatures detection can be affected by the underlying assumption that life elsewhere in the Universe would be based on a chemistry similar to the terrestrial one.
Being the building units of proteins, amino acids are high priority targets in the search for biosignatures. However, meteoritic samples exhibit a large set of amino acids, most of them unknown to our biosphere [2,3], suggesting that amino acids are not unambiguous indicators of life. Recently, concepts as "complexity" are being proposed for the development of new strategies for biosignatures detection, with no assumption on the underlying biology [4,5].

1.1 Selected amino acids and Computational approach

We analyze the properties of the α-amino acids from the isoleucine series [2-amino3-methylpentanoic acid, CH_3CH_2-$CH(CH_3)$-$CH(NH_2)$-COOH]. Isoleucine contains two chiral C atoms and exists as two distinct compounds based on the spatial orientation of the substituents at those C atoms. The isomer with absolute configuration S at both carbons is the α-amino acids L-isoleucine (L-Ile), used for the proteins synthesis. Its enantiomer is D-isoleucine, and its diasteroimer is D-alloisoleucine (D-allo, with opposite chirality only at one C atom), both not found in living organisms. The enantiomer of the latter is L-alloisoleucine, not involved in protein synthesis but featured in plants and human plasma.
Structural and electronic properties have been calculated with Density Functional Theory (DFT) and employing also higher methods to obtain more accurate ionization potential (IP) and electron affinity (EA) for the gas phase molecules and their forms as extracted from the solids. A complexity measure (from Lopez-Ruiz, Mancini, Calbet [6], C_{LMC}) based on the Shannon entropy of the electronic distribution (a general measure of randomness of the distribution) and on the disequilibrium of the distribution (quantifying the departure from uniformity), H-bond properties and a chirality index (Continuous Chirality Measure, CCM measuring the distance from the closest achiral object), have been calculated.

2. Results

The results show that for L-isoleucine and D-alloisoleucine, the forms extracted from the condensed phase (Fig. 1b,c and Fig. 1e,f), which are more similar to the ones acquired in a liquid fisiological solution, have lower gap (distance in energy between occupied and uncopied states, determining reactivity, polarizability and spectroscopic properties) with respect to the gas phase molecules (Fig. 1a and Fig. 1b) and that their complexity is higher (see Fig. 2). Complexity is not always correlated in a straightforward manner to the chirality index. L-isoleucine exhibits slightly higher complexity and acquires a higher chirality degree upon condensation when averaging over forms A and B in the condensate. In the context of molecular configurations, entropy is the degree of symmetry (in an ensemble of molecular configurations or in relation to the electronic distribution) and information is the degree of non symmetry. On the basis of order/entropy arguments, L-isoleucine would allow to store more information than D-alloisoleucine, despite a simpler H-bond pattern.

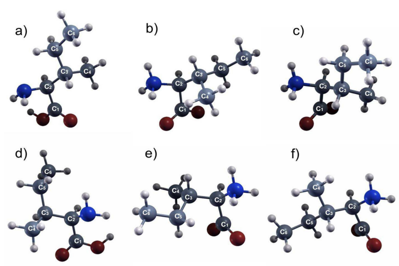

Figure 1: a) L-isoleucine in the gas phase; b) and c) forms of L-isoleucine in the condensed phase; d) D-alloisoleucine in the gas phase; e) and f) forms of D-alloisoleucine in the condensed phase

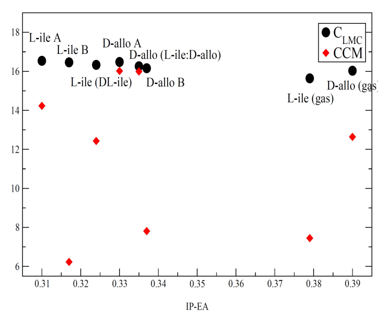

Figure 2: Complexity C_{LMC} and Chirality CCM vs the gap values for L-isoleucine and D-allosioleucine in the condensed and gas phase (a.u. are used).

3. Summary and Conclusions

The results show intriguing correlations among properties of the (few) amino acids here considered and might serve to design new strategies for biosignatures detection, allowing for a mean to score known and unknown amino acids on a universal complexity, electronic, bonding properties scale. A threshold might be identified in the relationship entropy/disorder and electronic properties, expressing propensity for charge transfer, beyond which complex molecules are unlikely to support the development of a full biological machinery. At fixed computational effort, this approach can be used for a large groups of molecules, also for those for which spectroscopic lines are not known.

Acknowledgements

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Effects of low and high energy proton radiation on the preservation of biomolecules as followed by their immuno-identification behavior

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Abstract

Bio-affinity based systems, such as antigen-antibody interactions, have been proposed for searching for molecular biomarkers in planetary exploration. However, the surface of planets and moons with little or no atmosphere are generally unprotected from the high-energy ionizing radiation that may severely affect the structure and chemistry of potential biopolymers. To understand what range of energy and proton radiation doses may be more harmful to the target biomarkers, we performed fluorescent immunoassays to monitor the radiolytic effect on target epitopes (the part of the molecule to which antibodies bind) exposed to low (5.5 kGy and 7 kGy) and high doses (55 kGy and 70 kGy) of 3 MeV and 200 MeV of protons. The effect of proton radiation was monitored by measuring the loss in the immuno-identification of target molecules due to the impaired ability of the antibodies for binding their corresponding radiation-damaged epitopes.

1. Introduction

The search for signs of past or present life in planets and moons of our Solar System is one of the great challenges of the upcoming space missions. On planetary environments, potential biogenic organic molecules would be exposed to chemical and physical degradation due to environmental factors. The ionizing radiation, one of the most pervasive long-term agents of organic molecule degradation, is in the form of galactic cosmic rays (GCR) and solar energetic particles (SEP) on planetary surfaces. During the last two decades, immunosensors (bioaffinity-based biosensors using antibodies) have been proposed for life detection in planetary exploration [1] and studies on the stability of antibodies have been performed to demonstrate the possibility of their use in a mission to Mars [2, 3]. In this context, it is critical to know how a long-term exposure to ionizing radiation may affect the integrity of potential organic molecular targets.

2. Material and Methods

We selected several organic molecules and a whole microorganism that might be potential indicators of extant or extinct life on Mars. All of them were immobilized on epoxy-activated glass slides and exposed to high energy protons (3 and 200 MeV) at radiation doses equivalent to 100-500 Kyr and 1-5 Myr of exposure at 1 m of the Martian surface based on MSL data [4]. Direct immunoassays were performed to test the structural integrity and preservation of epitopes in the printed biomolecules through the recognition of their corresponding antibodies.

3. Results

Results of two-way ANOVA revealed statistical differences in the immuno-identification of the immobilized molecules as a function of the dose, the energy and the interaction of both factors, which means that the dose caused effects in a different manner as a function of the energy. Also, two-way ANOVA results showed that the energy was the most powerful factor for 56% (9/16) of the immobilized molecules and the dose in the case of *B. subtilis* spores, EPS, LPS, FtsZ, rubredoxin, AEKAC and p-azo-L-Phe (44% of the immobilized molecules). Multiple range tests were performed to test the effect of the dose for each level of energy. These tests revealed that the differences as a function of the dose were higher at the lowest energy, showing all the immobilized molecules, except the bacterioferritin, significant effects with respect to the control at an energy of 3 MeV (Fig. 1A), whereas only 25% (4/16) of the immobilized molecules in the case of irradiation with 200 MeV (Fig. 1B).

After exposure to the lowest dose at 3 MeV, only one molecule (p-azo-L-Phe) lost a statistically significant portion of the original immuno-identification, whereas 31% (5/16) (GroEL, FtsZ, rubredoxin, AEKAC and Cys) surprisingly increased their immuno-identification signal (Fig. 1A). Under the lowest dose and 200 MeV, two molecules (AEKAC and LPS) lost and increased a significant portion of the original immuno-identification, respectively (Fig. 1B). Finally, after exposure to the highest dose, 75% (12/16) and 6% (1/16) of the immobilized molecules showed significant loss of immuno-identification at an energy of 3 and 200 MeV, respectively (Fig. 1). Three molecules (LPS, FtsZ and bacterioferritin) increased significantly their immuno-identification signal after irradiation with the highest dose at 200 MeV. However, no molecules increased its immuno-identification after irradiation with the highest dose at an energy of 3 MeV (Fig. 1A). After irradiation at the highest dose with protons of 3 MeV and 200 MeV, 25% and 94% of the tested molecules retained more 75% of their non-irradiated control immuno-identification signal, respectively (Fig. 1). On the other hand, T-tests were performed to evaluate the effect of the energy for the low and high doses. These results revealed statistically significant differences among the mean values corresponded to the two levels of energy for low doses and high doses in only 31% (5/16) of the molecules (GroEL, p-azo-L-Phe, Cys, LPS and cAMP). However, 18% (3/16) and 50% (8/16) of the molecules only showed significant differences among the two energies for the lower and the higher doses, respectively.

4. Figures

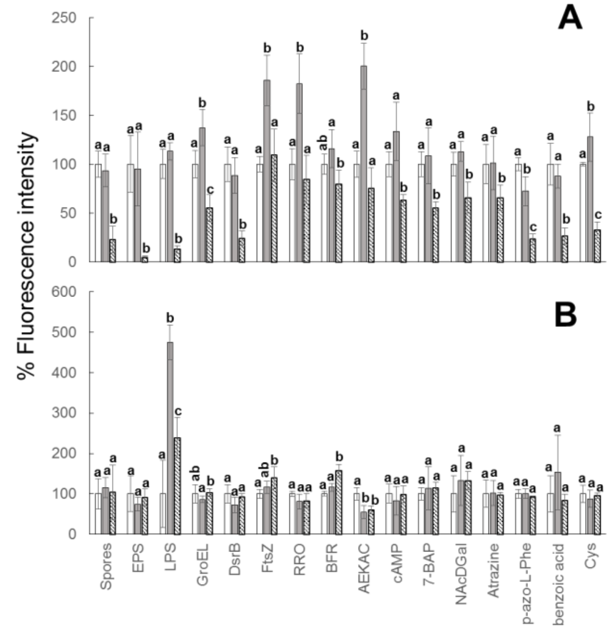

Fig. 1: Effect of proton radiation on the immobilized organic molecules. Average of the fluorescence intensity of spots containing each organic molecule after performing direct fluorescent immunoassays relativized to their respective non-irradiated control (considered as 100% of the signal). Non-irradiated samples (white bars), irradiated at low doses (5.5 kGy and 7 kGy) (grey) and irradiated at high doses (55 kGy and 70 kGy) (hatched) at energies of 3 MeV **(A)** and 200 MeV **(B)**. Letters represent statistical differences with respect to the control (0 kGy), that is, samples with the same letter are not significantly different ($p \geq 0.05$) based on Tamhane´s T2 or Bonferroni's multiple range tests.

5. Summary and conclusions

Our results revealed that the effects produced by a particular dose strongly depended on the proton energy. Also, we found a strong correlation between the radiolysis rates and the protons stopping power, related to LET (Linear Energy Transfer). We conclude that although unprotected planetary surfaces as Europa and Mars receive high energy (>100 MeV) protons, are those of lower energies (<10 MeV) the most harmful for biopolymers and on which future studies should mainly focus in.

Acknowledgements

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Diverse Stratosphere Circulation in tidally locked Exo-Earths

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Abstract

Stratosphere circulation is important to interpret abundances of e.g. photo-chemically produced compounds like ozone that we aim to observe to assess habitability of exoplanets. We thus investigate a tidally locked ExoEarth scenario for a hypothetical TRAPPIST-1b-like planet around an even cooler host star [1], TRAPPIST-1d [1], Proxima Centauri b [2] and GJ 667 C f [3] with a simplified 3D atmosphere model.

We show that the circulation in a transient stratosphere on these planets can be very diverse for these planets, ranging from a scenario with efficient equator-to-polewards circulation to the exact opposite, 'Anti-Brewer-Dobson'-circulation that confines air masses to the stratospheric equatorial region [4].

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Appraisal of lithologies and biosignatures using the ExoMars 2020 CLUPI instrument: blind tests using simulated mission observational conditions

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Abstract

The objective of the ExoMars 2020 mission will be the characterization of an ancient Martian locality with high potential for both former habitability and the exceptional preservation of physical and chemical biosignatures. The payload will include a drill producing cores from the subsurface, which will be imaged at high-resolution by the CLose UP Imager (CLUPI), an approximation of a geologist's hand lens. CLUPI will image with a maximum resolution of 7µm/pixel the physical character of the extracted core, from which immediate detailed geological observations can be made. In this study, we produced core samples of Mars-analogue rocks from the International Space Analogue Rockstore (ISAR) and, using a camera with observational settings prescribed to those of the CLUPI instrument, attempted a full characterisation of the samples. These samples were of lithologies, and featured biosignatures, analogous to those known or proposed for Mars. Images were taken in PanCam- and CLUPI-representative conditions. These images were analysed in a "blind test" against a directed analytical 'questionnaire' by a group of scientists. Their conclusions are indicative of the potential of the CLUPI instrument to make fundamental geological assessments of samples prior to their analysis by the Pasteur Instrument Suite.

1. Introduction

Astrobiology on Mars has a long and intriguing history; since the *Viking* missions of the mid-1970s, a number of subsequent spacecraft have explored the planet with explicit objectives relating to the detection of life. The ESA-Roscosmos ExoMars 2020 missions [1,2], to be launched in 2020, will target an ancient locality on Mars within which past (Noachian) habitability would have been possible. More than 3.5 Ga have passed since the deposition of these rocks and, despite the apparent possibility for enhanced lithological preservation on Mars, the most appropriate analogue for planetary habitability over such great geological time and at microbial scales is the early Earth [3,4].

The International Space Analogue Rockstore (ISAR; [5]) was created as a tool for mission preparation, including geological samples representative of the expected lithologies on Mars, and examples of samples from the early Earth within which biosignatures of putative chemosynthetic origin are preserved. These biosignatures, though often enigmatic in their morphological preservation, present traces that can be identified as biogenic in origin. Chemosynthetic pathways represent the most likely metabolic affinities for putative extinct (or extant) Martian life [2,3].

A selection of eight of the ISAR samples relevant to Martian geology [5] and astrobiology were chosen for use in this "blind test".

2. The CLUPI "Blind Test 2.0"

When cores are taken by the ExoMars 2020 rover, the first step of geological analysis will be conducted by the CLUPI instrument, which will essentially function as a geologist's hand lens [6]. From these analyses, *conducted on core samples*, will come the initial interpretations of the small-scale (textural and rock fabric) geology of the sample, and the initial estimation of morphological biosignatures that may be preserved within. These initial findings will guide the strategy of analysis to be undertaken by the Pasteur Instrument Suite.

Following the undertakings of the first “blind test” [7], the objectives of this new “blind test” concern the direct appraisal of the cores collected by ExoMars 2020. The observation of samples in core form will add further limitations to the possibility for imaging and interpretation. Cores were produced of representative size (3cm x 1cm) to those that will be produced during the mission and were imaged using a camera setup imitating the conditions of imaging of PanCam and CLUPI. A set images of the cores were taken in different lighting conditions and at a range of resolutions including the maximum expected for the CLUPI instrument (7µm/pixel; [6]).

An analytical ‘questionnaire’ was designed and sent, together with the images and a set of Raman spectra, to a group of scientists. These data were sent sequentially such that the scientists could modify and develop their ideas as more data became available. This ‘questionnaire’ probed for initial observations of mineralogy, texture, sedimentary structures and biosignatures, together with fundamental geological observations including grain size, grain morphology, secondary alteration phases and features, impacts of porosity, deformation and microtectonics, and finally an estimation of the identity of the sample.

The results of the questionnaire showed that, although biosignatures and sedimentary structures could be challenging to successfully identify in the limited image set, many of the fundamental geological observations were made with success. The analytical workflow suggested by the questionnaire is clearly an appropriate approach to be taken in preliminary analyses. When combined with the detailed analytical work to be conducted by the remainder of the Pasteur Instrument suite, a truly detailed appraisal of the palaeoenvironment and geological history should be feasible.

3. Summary and Conclusions

The “Blind Test 2.0” has measurably added to the findings of the first “blind test” by introducing limitations in findings that will be incurred by the nature of the sample, i.e. it is more difficult to make concrete geological conclusions from a sample with core-like dimensions as opposed to a hand sample. To this end, discussions of the shortcomings in observation of small samples imaged in limiting conditions are critical to the geological interpretation, particularly for heterogeneous samples, for which CLUPI may be unable to representative image. The limitations of image resolution and the challenge in detecting primitive biosignatures add further constraints to our observations.

Nevertheless, the positive outcome of the “Blind Test 2.0”, i.e. that many detailed geological, textural and mineralogical observations can be made from only the PanCam and CLUPI images together, is indicative of the utility of this instrument in the payload, particularly in initial guiding observation of the samples taken. Together with recent findings that aspects of palaeoenvironmental reconstruction may be achieved through morphometric analysis of the shape parameters of grains within the resolution limits of CLUPI [8], the images taken will provide important evidence for geological interpretation.

The “Blind Test 2.0” is just one in a series of planned tests of CLUPI together with the other instruments in the Pasteur payload, the results of which combined will continue to guide the the sampling and analysis stratagem of the ExoMars 2020 rover. Testing campaigns such as these will define if, and how, putative Martian biosignatures may be detected in samples collected at the surface of Mars.

Acknowledgements

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Photoprocessing of formamide ice: route towards prebiotic chemistry in space

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Abstract

Formamide (HCONH2) is the simplest molecule containing the peptide linkage of crucial importance in prebiotic chemistry and physics in the fascinating open questions of modern science about the origin of life. These peptide links are known to be the basis for assembling proteins and polypeptides from amino acids with a crucial role in the biotic processes of Earth life, as was argued by a recent study by Saladino et al. (2012) [1]. Formamide was observed in the interstellar medium and it's a molecule very important for its active role in prebiotic chemistry, because the chemical reactions of molecules like Formamide containing H,C,N and O are considered a plausible pathway for synthesis on the Earth of biomolecules under prebiotic conditions [2]. For these reasons, the Formamide is of great interest for astrochemists and astrobiologist and many experimental and theoretical studies have been carried out in order to understand the physical and chemical properties of Formamide under space conditions.

Formamide was first detected in the gas phase in Orion-KL and SgrB2 (Turner 1991 [3]; Nummelin 1998 [4]; Halfen 2011 [5]), but it is possible that the Formamide, observed in the gaseous phase, is initially absorbed on the surface of the grains of the ISM and then evaporates as a consequence of the radiation coming from the stars.

1. Laboratory work

The goal of our laboratory work is to study the Formamide under simulated astrophysical conditions such as UV irradiation at low temperature. In laboratory we can carry out experiments at 65 K irradiating with UV-Enhanced Xenon lamp, a good simulator of the radiation of solar type stars. We report two analysis. The first is UV irradiation of pure Formamide samples and Formamide adsorbed on various space relevant minerals, like forsterite, pyrite and TiO2, at 65 K investigated by infrared spectroscopy (FTIR) in order to understand the photostability of Formamide under simulated space condition. The second analysis is carried out in ultra-high vacuum chamber to investigate the same process of UV irradiation of pure Formamide by mass spectrometry and Temperature Programmed Desorption (TPD) in order to understand the physical properties during the photo-destruction process in simulated space conditions.

2. Results

We have seen that during the irradiation some bands of the spectra are reduced, like the band at 1721 cm^{-1}, assigned to CO stretching. Through the analysis of the TPD curves it is seen that the pure Formamide splits into NH2, HCO and CH2NO. We have analyzed these fragments after 5 hours of irradiation and what we notice is that they sublimate before Formamide (the Formamide subimates at 220 K, HCO and NH2 at 184 K and CH2NO at 182 K). After 5 hours of UV irradiation, we have not seen the synthesis of more complex molecules, both in UHV and when the Formamide is absorbed on minerals. These results allows us to take a step forward on the knowledge of the physical and chemical properties of the Formamide in space.

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Dallol: A unique study of life under multiple co-occurring physiochemical extremes

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Abstract

While studies have been conducted on microbial communities inhabiting extreme environments, few studies have focused on sites with multiple physiochemical extremes. Dallol is a unique location for the study of the limits of life at the triple juncture of high temperature, low pH, and hypersaline extremes. This project aims to characterize the phylogeny and physiological adaptations of microbes inhabiting the Dallol hydrothermal system. Samples were collected from two outflows located in the main Dallol outcrop. Microscopy results from samples are inconclusive, with some very cell-like morphologies. Both anaerobic and aerobic enrichments have been carried out for the isolation of novel microorganisms. DNA has been successfully extracted and the amplified 16S rRNA gene will be sequenced.

1. Introduction

Studying environments exhibiting physiochemical extremes is key to understanding the limits of life. While studies have investigated physiochemical extremes in isolation, few have examined the effect of multiple co-occuring physiochemical extremes on microbial diversity [1]. Dallol represents a unique site to study the limits of life because it exhibits three physiochemical extremes simultaneously: low pH, high temperature, and salinity.

2. Geological Context

The main outcrop is located above a salt succession that is at least 900 meters thick [2]. Local fluids spring out at the surface (Figure 1,2) have mixed magmatic and meteoric origins [3]. As the water is heated, it passes through halite-dominated lithology that characterizes the surrounding area [2], becoming supersaturated in salts such as NaCl and $MgCl_2$.

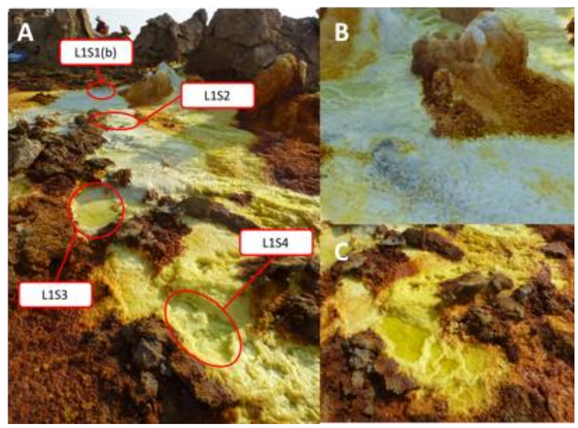

Figure 1: (a) Location 1 (L1) sampling site overview; (b) outflow source; (c) L1S4 site on Day 1 (D1)

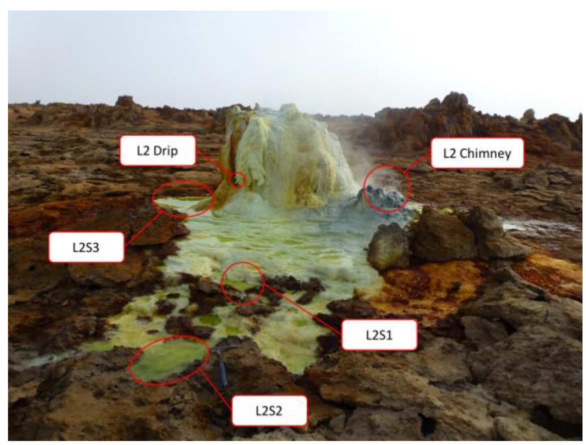

Figure 2: An overview of the Location 2 (L2) sampling site on the main outcrop

The field pH meter could not measure pH values below zero, so pH was re-measured in the laboratory upon return, as was water activity. The temperature was measured in the field. Environmental parameters were measured for both sample locations (Table 1).

Sample ID	pH	Temp	DO (mmHg)	A_w
Location 1				
L1S1D1	-0.30	68°C	51	0.714
L1S1D2	-0.33	-	-	0.710
L1S2	-0.34	44°C	30.5	0.710
L1S3D1	-0.34	40°C	200	0.709
L1S3D2	-0.37	-	-	0.708
L1S4	-0.40	35°C	150	0.710
Location 2				
L2 drip	-0.37	80°C	-	0.712
L2S1	-0.38	31.7°C	76.4	0.710
L2S2	-0.42	31.0°C	70.3	0.707
L2S3	-0.43	33.3°C	66.6	0.707

ICP-OES results indicate a NaCl-dominated, kosmotrophic environment with molar salt concentrations (±10% w/v).

3. Cultivation

Given the inconsistent dissolved oxygen readings in the field, aerobic and anaerobic enrichments were set up parallel by adding yeast extract. After several weeks, the aerobic cultures began to differentiate with regards to colour and opacity. The differentiated cultures were subcultured into pH-adjusted media. the original sample material as well as subcultures was visualized (Figure 3).

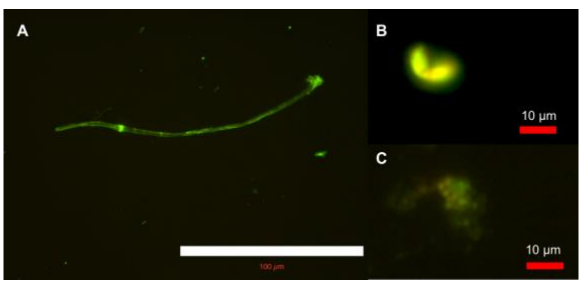

Figure 3: Summary of the morphologies observed in original sample (a) and subcultures (b,c). White scale bar represents 100 nm

6. Summary and Conclusions

The geochemical analyses carried out thus far confirm that the Dallol environment exhibits a triple junction of extremes (pH <0, temperature ≥ 30°C, salinity ≥ 10%). Further geochemical characterization is planned to characterize the mineralogical composition of the salt crusts in order to determine its effect on the fluid composition.

While microscope analysis of the original samples from Dallol provided evidence for structures that were an order of magnitude larger than prokaryotic cells, these may be microbially-mediated, formed to create a more habitable microclimate under such extreme conditions. Future work will investigate whether these structures were formed under microbial influence. Microscope analyses of the subcultures showed cell-like structures between 1 and 15 µm in diameter. However, given the lack of cell motility it is possible that these cells are not actively metabolizing. Sequencing of DNA extracted from the samples will determine which microbes are present in the samples collected.

Given the visualization of biotic and cell-like structures at various scales, it seems likely that there is microbial matter in these samples. This is increased evidence that life may be able to survive at the triple juncture of high temperature, low pH, and hypersaline conditions as seen in Dallol.

Acknowledgements

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Zag-Monahans relation to Comets and Biotic Chemicals

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Abstract

The halite crystals in the Zag and Monahans meteorites dated at 4.5Gyr and containing complex organics in brine inclusions provide vital data from the early solar system. We argue their origin is likely to be early comets. Their organics would derive from interstellar grains in the pre-solar nebula and from pre-biotic or biotic processing in the first 1-10Myr after the comet accretion.

1. Indications of Biotic Materials in Comets

Astronomical arguments in favour of complex organics in comets, summarised recently in Steele et al [1], go back to 1975.
The Giotto and Vega space-probes to Halley's comet in 1986 fatally ruptured Whipple's "dirty snowball" cometary paradigm, finding its surface to be very dark and its dust to be high in carbonaceous compounds. Imaging of comet nuclei on fly-by missions and the landing by Philae of the Rosetta mission to comet 67P have established that comets have substantial crusts, processed by insolation, micro-impacts and outgassing. It follows that the cometary material and organics detected from afar are substantially processes and far from the "pristine" nature predicted.

2. Water on Comets as bio-habitat

Comets have been largely dismissed as a habitat for life, seeing their temperatures are well below that of liquid water. But there are exceptions. Radiogenic heating is expected to have melted the interiors of larger early comets for a few Myr post accretion. Accreted material included interstellar organic grains and any viable spores, would have been processed and aqueous-altered in the interior, while gases escaping though the surrounding 'snow' would have fractionated and crystallised out.

Liquid water may be well below 273K, due to dissolved salts and anti-freeze organics, for which there is now direct evidence in brines and salt crystals. Moreover, some of the focus on "liquid" has been misleading, as cracks in ice are found to be high in anti-freeze contaminants in which metabolism in microorganisms can still proceed, slowly, as low as 230K. Comet 97/P generated a coma at 3.9AU. Comet observations have of course established that the sun significantly warms the daytime sub-solar surface, and particularly the dark surface with low IR emissivity of comets. Emissions through cracks in 97/P were seen to be very sensitive to solar orientation. Evidently cracks open and refreeze with changing solar illumination.

3. Halite Crystals in the Zag and Monahans meteorites

Both these 1998 meteorites are regolith breccias containing mm-sized halite crystals (NaCl; KCl), blue in colour due to extensive cosmic-ray processing. Rubin et al [3] identified shock metamorphism, thermal metamorphism and aqueous alteration on the asteroid (H-chondrite) parent body. Subsequent studies [7] found µm-sized zones of complex mixtures of primitive organics (aliphatic, aromatic/olefinic, vinyl-keto, carboxyl/ester and carbonate) .

Recently Chan et al. [1] made a comprehensive analysis of soluble and insoluble organic compounds trapped in brine inclusions in the mm-sized halite crystals. They summarised them as organic precursors, intermediates and reaction products that make up precursor bio-molecules such as amino acids. The organic compounds also contain a mixture of C-, O-, and N-bearing macromolecular carbon materials, including aromatics, ketones and imine or imidazole compounds.

Their data showed nitrogen ^{15}N is enriched but carbon ^{13}C is depleted. Enrichment compared with solar system values can arise from preferential retention on partial evaporation to space, whereas depletion of ^{13}C is normally taken as indicative of biological fixing processes. A C-rich area of Monahans was found as $\delta^{13}C=37.6+/-4.2\ ^{o}/_{oo}$, mid-range for terrestrial biological carbon ($\delta^{13}C$ =

25-60 $^{o}/_{oo}$) whereas C-rich meteorites Murchison and Orgeil are less depleted $\delta^{13}C$ ~17-19$^{o}/_{oo}$

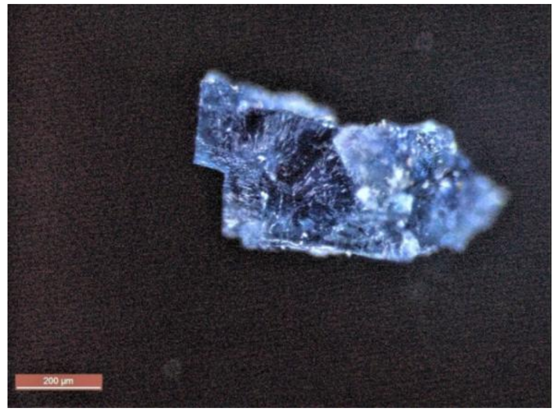
3. Comets as a source of organic-rich brines within halite crystals

Astronomical arguments in favour of complex organics in comets, summarised recently in Steele et al [4], go back to 1975. Interstellar organics from the pre-solar nebula together with any debris from living matter, spores etc. would be accreted on the early comets. Space probes to Halley's comet in 1986 established its dust as high in carbonaceous compounds and its surface as very dark, challenging Whipple's ‘dirty snowball’ comet model that was the reigning paradigm at the time. Imaging of comet nuclei on fly-by missions and the recent landing on 67P by Philae in the Rosetta mission have established comets to have coherent crusts, processed by insolation, micro-impacts and outgassing [6]. Beneath the crust, we infer temporary gassy regions, even pools [5] which, as they freeze and gradually lose H_2O, concentrate the biotic and pre-biotic organics in brines. We suggest this as a source of micron-scale halite crystals in current-day comets, but they would not survive long in free space.

4. Summary

The organics in the brine inclusions of the Zag and Monahans meteorites’ halite crystals look like the closest to ‘pristine’ cometary matter found so far. They contain biotic or pre-biotic chemicals in the first 100Myr of comets. The analyses are compatible with previous studies of cometary organics, but the meteorite case shows a more complex suite of compounds, indicative of biotic organics. The ^{13}C depletion is particularly indicative of biotic rather than pre-biotic chemistry; if confirmed, it would be highly significant, implying comets were endowed from birth with micro-organisms able to colonise the icy cometary environment, as they colonise terrestrial antarctic snows. The comet timescale was of course far longer, ~10-100 Myr after the initial radiogenic heating decayed away.

5. Figures



Blue halite crystal from Monahan [1]

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Analog Mass Spectra of Astrobiologically Relevant Organic Material for Spaceborne Mass Spectrometers and their Future Implications

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Abstract

Characterizing the abundances of various amino acids, peptides and fatty acids is fundamental in the search for extraterrestrial life. For future space mission these investigations are possible with in situ space detectors [1] [5] that assess the abundances of these key species in ice grains potentially emerging from ocean bearing moons like Europa and Enceladus [3] [4]. Distinguishing biotic and abiotic fingerprints of these organic substances is crucial to further enhance the possibilities in interpreting mass spectra of ice grains in space.

With our worldwide unique experimental setup we are able to reproduce mass spectra of amino acids, peptides and fatty acids in ice grains. We simulate the impact ionization mechanism in space by an infrared laser intersecting an ultrathin water beam. The resulting spectra have been demonstrated to be highly comparable to those of ice grains detected by impact ionization space detectors like the Cosmic Dust Analyzer (CDA) on board the recently ended Cassini mission and the Surface Dust Analyser (SUDA) on board the future Europa Clipper mission [2]. The experimental setup (IR-FL-MALDI-ToF-MS) consists of a vacuum chamber ($\approx 5 \times 10^{-5}$ mbar) in which a water beam (radius of 7 – 9 µm) with dissolved chemicals therein is inserted. Mixtures of other solvents like methanol and acetonitrile with water can also be used and, therefore, all water soluble and many water insoluble substances can be analyzed. A pulsed infrared laser (λ = 2840 nm) hits the beam of the aqueous solution. In this way cations, anions, electrons and neutral molecules of the solvent and the dissolved substances therein are created. The cations as well as the anions can be analyzed in a commercial ToF-MS. The setup will be upgraded in future with an additional ultraviolet laser to subsequently ionize the neutral molecules that can then be analyzed in the same ToF unit.

Our laboratory results show a high sensitivity on the tested substances. The detection limits of salts and organics are in the ppm or even ppb range. Different amounts of the analytes lead to different intensities of the related peaks in the mass spectra. We are able to easily differentiate between biotic and abiotic signatures of amino acids and fatty acids in the analog spectra. Peptides can also be reliably characterized. By comparing the laboratory results with spacecraft data we have the ability to recognize and distinguish such signatures in ice grains from icy moons with a subsurface ocean. We are currently developing a comprehensive spectral reference library for in situ space detectors from a wide variety of organic analog materials in icy grains.

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The European Astrobiology Institute

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Abstract

The European Astrobiology Institute (EAI) will be a consortium of European research and higher education institutions and organisations as well as other stakeholders aiming to carry out research, training, outreach and dissemination activities in astrobiology in a comprehensive and coordinated manner and thereby securing a leading role of the European Research Area in the field.

1. Introduction

Fundamental questions in science like “How and when did life emerge on Earth?”, “How did our solar system and life evolve and how will it develop in the future” and “Is there life on other celestial bodies” will not be answered by one discipline alone but require a concerted and coordinated approach involving many researchers with seemingly unrelated scientific backgrounds. Also, the European research landscape is rapidly changing on a global scale. Boundaries between disciplines disappear and new cross-disciplinary fields emerge. Astrobiology is one of them. Research in such field requires interaction and exchange of ideas and new results between scientists from many countries and fields, something that only larger research communities like the European Research Area can accomplish. In order to take astrobiology-related research forward and to prevent a counterproductive fragmentation of the European Astrobiology research community through duplicate or excessively overlapping initiatives and structures the AstroMap Report (drawn up under the EU FP7 programme) unequivocally recommends the creation of a pan-European platform for research, training outreach and dissemination in Astrobiology. The European Astrobiology Institute (EAI) aims to function as such an entity. Such an institute is required to keep Europe’s leading position in this interdisciplinary field relatively to other countries and regions. EAI will closely collaborate with several related European organizations including ESA, EANA, Europlanet etc. but as a network of institutions fundamentally differs from existing bodies.

2. Proposed aims of the EAI

The EAI will have the following aims:

- Perform ground-breaking research on key scientific questions in astrobiology (which will be periodically reviewed) requiring a cooperative interdisciplinary approach.
- Disseminate high-quality results of these efforts effectively in the scientific community
- Provide interdisciplinary training for students and early career scientists in astrobiology
- Engage in education on astrobiology on all levels
- Liaise with industry to foster collaborate on technological developments that are relevant to astrobiology research and beneficial to Europe as a whole
- Coordinate outreach activities of European astrobiologists to the general public, industry and all other relevant stakeholders.
- Act as advisory body and provide high-quality expertise to European research organisations and decision makers
- Ensure the necessary financial means to carry out these activities through a coordinated approach to European funding agencies.

2.2 Scientific key areas and questions to be tackled by the EAI

The following scientific areas are proposed to be tackled by the European Astrobiology Institute:

- Formation of planetary systems and detection of habitable planets and moons
- Co-evolution of early Earth's geosphere, atmosphere and biosphere
- Early life and life under extreme conditions
- The pathway to complexity: From simple molecules to first life
- Search for life in early and extreme terrestrial environments and on other planets
- Historical, philosophical, societal and ethical issues in astrobiology

All these fundamental research questions require a concerted effort by scientists from different fields.

3. Proposed activities of the EAI

To achieve the above-mentioned aims, the following activities are planned by the EAI:

- Foster interdisciplinary research projects in the field, especially by early career scientists
- Hold high-level general conferences in astrobiology as well as smaller workshops on specific subjects to provide a forum to discuss and plan innovative research projects
- Enable and facilitate access to European research infrastructures and field sites for astrobiologists and organise expeditions to such sites
- Provide a comprehensive multidisciplinary European astrobiology training for students and early career scientists offering both basic and specialised training events in the field as well as training in generic skills (proposal writing, planning of scientific projects) and a mentoring programme
- Organise web-streamed seminars by leading scientists in astrobiology, and also provide an interface (web based tools) to collect and share astrobiology lectures.
- Create a network for astrobiology education and provide training material for basic, secondary and higher education in Europe.
- Produce high quality reference works (e.g. the Encyclopedia of Astrobiology).
- Create and effectively promote excellent outreach material in cooperation with entities engaged in public education (museums, schools and adult training centres).
- Promote contacts to media and ensure high quality coverage of astrobiology-related European research by maintaining an expert pool which journalists can contact.
- Use the wide interest of the general public to coordinate and promote involvement of citizen scientists in astrobiology research projects.
- Create a team for liaison between research and industry with representatives on both sides.
- Approach and inform decision makers in governmental and non-governmental organisations about astrobiology research in Europe.
- Formulate and continuously update a long-term planning of a research strategy in astrobiology for the European Research Area.
- Coordinate the approach to funding agencies to finance the activities of EAI and astrobiology research in the European Research Area
- Include both "top level researchers" and early career scientists in all activities.
- Act as a strong voice for the European astrobiology community.
- Collaborate with astrobiology networks and institutes outside Europe Area.

4. Current state of preparation

An Interim Board was formed consisting of members and employees of the main stakeholders in this field in the European Research Area (ESA, ESF, ISSI, EANA, German Aerospace Centre, CNRS, CNES, INAF, Europlanet, etc.) to prepare the creation of the EAI. It has elaborated a draft Action Plan mapping out the tasks, structure, governing bodies, activities, funding and administration of the EAI. This Action Plan is to be discussed with the whole European astrobiology community during the summer of 2018. Recruitment of institutions will take place in autumn and winter 2018/19 and the launch of the EAI is planned for spring 2019.

Documents and further information about the EAI as well as instructions how to join the discussion forum will be available at the website http://www.europeanastrobiology.eu.