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The Astrobiology Laboratory in Arcetri: past and present activities to search for signs of life in space

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Abstract. Laboratory simulations on synthesis and stability of biomarkers under space-like conditions provide hints on their stability and preservation in space. These studies contribute to support the scientific activity and technology development of life detection instruments. A systematic study of the effects of UV radiation on a variety of molecule-mineral complexes have been carried on over the years at the INAF Astrobiology Laboratory in Arcetri Firenze. Many different prebiotic and bio-molecules have been studied in our laboratory starting from interstellar complex organic molecules (iCOMs) present in protoplanetary disks such as formamide, acetonitrile, acetaldehyde, to more complex molecules likely present on solar system objects such as PAHs, amino acids, nucleobases, nucleosides, nucleotides and, finally, the biological compounds melanine and parietin. Such molecular compounds have been adsorbed onto the surface of various space relevant minerals, i.e. metal oxides and sulfides, silicates and apatites (forsterite, enstatite, antigorite, lizardite, spinel and pyrite etc), and analyzed under space-like conditions. Comparing protective/catalytic effects of various minerals and testing the sensitivity of different techniques for detection of the diagnostic features of biomarkers embedded into mineral matrices as function of the biomarker concentration, helps to unravel the role of rocky surfaces in the origin of life and provides hints for the search of organics in present and future robotic space exploration missions. Moreover, the laboratory in Arcetri is involved in astrobiology space mission instrument development and test, as well as planetary protection activities to prevent organic contamination both back and forward during space mission towards astrobiological relevant target.

Key words. Astrobiology – Laboratory – Biomarkers – UV irradiation – ISM: iCOMs – Protoplanetary Disks – CubeSat – Planetary Protection

1. Introduction

Laboratory simulations on synthesis and stability of biomarkers under space-like conditions provide hints on their stability and preservation in space. These studies contribute to support the scientific activity and technology development of life detection instruments. Mineral surfaces are energetic environments that can assist prebiotic organization by adsorbing selected molecules and allowing their concentration and chemical evolution, possibly toward complex (pre)biological systems (Brucato & Fornaro 2019). This dynamic rocky environment can also play a crucial role as promoter of chemical reactions towards increasing molecular complexity. Moreover, the presence of minerals can mediate the effects of electromagnetic radiation and influence molecular photostability, catalyzing photoreaction or protecting molecules against degradation. This process assumes a pivotal role in protostellar environments where it can lead to the formation of "complex" organic molecules. Such interactions are responsible for the preservation/degradation mechanisms of organic molecules observed in all the planetary formation stages. In particular, the discovery of organic molecules on asteroids and comets confirms their role as transport and delivery vehicles of building blocks of life on Earth and possibly on other bodies of the Solar System. Moreover, the study of molecular biomarkers in a Martian-like environment allows us to explore the conditions for their detection by next NASA and ESA rovers that will explore the Martian surface and subsurface, namely Perseverance and Rosalind Franklin, respectively, and the selection of the most interesting samples to analyze in situ or/and collect for sample return.

2. Laboratory description

The Astrobiology Laboratory of the INAF-Astrophysical Observatory of Arcetri is currently hosted in the Garbasso historical building on the Arcetri hill (nowadays part of Department of Physics and Astronomy of the University of Florence). The laboratory hosts a series of physical and chemical instruments for astrobiological and planetological studies under simulated space conditions. A sample preparation and curation facility and an extensive collection of analog materials complement the laboratory resources. A series of instruments for mineral treatment is operated with protocols designed in the Arcetri laboratory in order to produce analogue planetary samples from natural minerals. Well-established procedures allow the production of powders, the selection in size of grains and the cleaning from organic contaminants. Arcetri laboratory science team is involved in production and analysis of analog samples in collaboration with other analytical laboratories around the word and space mission science teams. The lab is also equipped for the manipulation of meteorites and samples returned from space missions.

A complementary facility in the laboratory is designated for preparation and study of interaction between biomolecules and mineral matrix in the framework of biosignatures detection and survival. This includes selection of <10 micrometer grain size fractions as well as production of pressed pellets and adsorption of molecules with spike and kinetic processes (Fornaro et al. 2013a). Optical and IR microscopy with UV spectroscopy analysis are used to characterize the samples before and after preparation. Finally the Arcetri Astrobiology Laboratory hosts a complete series of instruments for powerful analytical analysis. Among the main experimental apparatus there are: FT-IR interferometer and microscope for transmission and reflectance IR spectroscopy, an Ultra-high vacuum chamber for gas chromatography mass spectroscopy and a LC-MS setup. In both FT-IR and high vacuum apparatus through thermal control from cryogenic to high temperatures and UV in-situ irradiation we can reproduce a wide range of extraterrestrial environments.

3. Scientific results overview

Many different prebiotic and bio-molecules have been studied in our laboratory starting from interstellar complex organic molecules (iCOMs) present in protoplanetary disks such as formamide, acetonitrile, acetaldehyde, to more complex molecules likely present on solar system objects such as PAHs, amino acids, nucleobases, nucleosides, nucleotides and, finally, the biological compounds melanine and parietin. The study of such molecular compounds interacting with the surface of various space relevant minerals, (i.e. metal oxides and sulfides, silicates and apatites) are pivotal to understand the route of prebiotic chemistry in planetary evolution and to interpret data from space missions exploring the Solar System in search of biosignatures. In the last few years we started a series of studies of prebiotic molecules (such as formamide $HCONH_2$) behaviour in high vacuum regimes under UV irradiation (Corazzi et al. 2020). We studied the thermal desorption process of pure formamide ice and in presence of TiO_2 dust, before and after UV irradiation through Temperature Programmed Desorption analysis. Through these experiments, it is possible to follow the thermal desorption of a given molecule and its fragments and constrain parameters such as the thermal desorption temperatures and the binding energies. Recently, we performed for the first time these kind of experiments in presence of silicate grains. We carried out the thermal desorption of astrophysical relevant ice mixtures of acetonitrile (CH_3CN), acetaldehyde (CH_3COH) and water from olivine grains, studying how the interactions between the molecules and the grain surfaces and the diffusion of the molecules on the surface mineral can influence the thermal desorption process and so the presence of interstellar molecules in gas phase (Corazzi et al. 2021). These studies are in support of the interpretation of molecule observations in star forming regions and hot corinos, where the thermal desorption is the responsible process for the sublimation of frozen mantles and so for the presence of molecules in gas phase.

Moving to more evolved planetary environment, the comparison of protective/catalytic effects of various minerals helps to unravel the role of rocky surfaces in the origin of life and provides hints for the search of organics in present and future robotic space exploration missions. The analyses of analog samples is pivotal to test the sensitivity of different techniques for detection of the diagnostic features of biomarkers embedded into mineral matrices as function of the biomarker concentration, and to support space mission aimed to find evidence of past and present life like Mars2020 and ExoMars2022. Several studies were conducted in the Arcetri Astrobiology Lab to evaluate the survival of biomolecules in presence of mineral matrices (Fornaro et al. 2013b,c; Fornaro et al. 2018, 2020; Potenti et al. 2018; Poggiali et al. 2020). Our results show that degradation under Martian-like conditions occurs much slower than in terrestrial ambient conditions. We investigated several minerals with different class of biomolecules: nucleotides, labradorite and natrolite mainly promote photodegradation, hematite and forsterite exhibit an intermediate degrading effect, while apatite, lizardite and antigorite do not show any significant catalytic effect on the degradation of the target organic species. Amino acids showed a lower photodegadation effect when adsorbed by antigorite and spinel compared with forsterite and pyrite. Our experimental results investigate a large class of molecules and mineral to unveil their intrinsic photostability. Last but not least our laboratory specialized over the years on the the study of molecule-mineral interactions, investigating experimentally the thermodynamics of the adsorption process through determination of the equilibrium adsorption isotherms.

Finding the cross-section for photodestruction can allow an evaluation of the survivability of organic molecules in space environments with different UV fluxes. It is interesting to compare the results obtained in this work with the exposition experiments that were made during the BIOPAN 6 mission launched on 14 September 2007 by ESA. A series of organic compounds were sent to low Earth orbit and their photodegradation measured Guan et al. 2010. Using a dedicated setup, glycine, adenine, guanine, xanthine, hypoxanthine, urea, polyC3O2 and polyHCN were exposed to solar radiation. The experiments performed in space were also duplicated in laboratory in simulated condition using as UV source a microwave-excited hydrogen flow lamp similar to Peeters et al. experiment, thus irradiating the sample with VUV photons dominated by Lyman-a emission. The results provided that the photostability of amino acids in space at 1 AU is an order of magnitude larger than that obtained in laboratory. The authors concluded that H2/He lamp is not a good simulator of UV spectrum. Interestingly, from the data of Guan et al. we can derive that the cross-section of photodegradation of adenine in space experiment is 1.8 $10^{2}0$ cm^2, value very similar to that derived in our studies. This suggests not only that our experiment is a good simulation of irradiation process in space, but also that the interaction with UV photons at energies corresponding to the adsorption bands in the range 200–300 nm is the major degradation mechanism.

The UV flux on Mars' surface is higher than on Earth, amino acids on Mars have a typical time of surviving of the order of hours. Laboratory studies with in-situ analysis by several on-going and future missions can give a direct confirmation of such results. Moreover the in-situ analysis can outline the way to be followed by the laboratory ones, in that high hopes are put on the future mission Exo-Mars, the probing of the subsoil is expected to give more insights regarding the organic molecules that can be found on Mars. If amino acids were on the martian subsoil and they are detected, it means that in some way they were formed and protected, so it will become necessary to understand how and why they are there, and if oligopeptides are found, it has to be understood the ways taken to polymerize. So, an ideal prosecution of this work would be to adapt all the analysis performed in this thesis with minerals that would be found on the sites that will be analysed by Exo-Mars. Generally speaking our work highlighted the importance, in the present and future searches for biomarkers on Mars and in the Solar System, of mineral composition as an important factor to be addressed for a positive detection.

Arcetri laboratory is also involved for management and functional test of AstroBio CubeSat (ABCS), a 3U CubeSat (100x100x340 mm) selected by European Space Agency (ESA) to be launched on fall 2020 with the Vega C qualification maiden flight, as piggy back of the ASI LARES2 satellite. ABCS will be deployed in an approximately circular orbit at 5900 km altitude and 70 degree of inclination spending a significant amount of the orbital period within the harsh internal Van Allen belt, close to its maximum. The CubeSat will host a laboratory payload based on an innovative lab-on chip technology suitable for research in astrobiology with the objective to test in space environment a highly integrated laboratory using immunoassay techniques exploiting chemiluminescence detection. Development of this kind of technology for space application will enable its usage in future astrobiology mission towards the Solar System (Brucato et al. 2020).

Finally, our laboratory is involved in several Planetary Protection activities, with the aim to avoid two possible ways of contamination in space exploration:

- Forward contamination could arise from spacecrafts launched for space exploration. Forward PP has the aim to avoid that terrestrial organisms and organic materials carried by these spacecrafts contaminate other celestial bodies in the Solar System (and consequently returned samples). This applies to both unrestricted and restricted missions.
- Backward contamination could arise from returned samples, brought back to Earth in a sample return mission. Backward PP has the aim to avoid any possible contamination of the Earth biosphere, due to extraterrestrial life or bioactive molecules. This applies to restricted missions, only.

Forward PP requires the sterilization of spacecrafts in order to reduce the possible bioburden (in particular, in landing operations) and the definition of flight plans able to avoid non-nominal impacts. Backward PP requires the definition of procedures and technologies to protect the Earth from returned extraterrestrial samples. Arcetri laboratory team members were involved in Planetary Protection for ExoMars2016 and 2022 missions. Moreover, we participated in several boards to establish international protocols to avoid contamination of outer Solar System in future missions trought the project "Planetary Protection of Outer Solar System (PPOSS)". This European Comission's H2020 funded project ended with the publication of an handbook on the state-of-the-art and good practices to implement planetary protection requirements (PPOSS Consortium

2018). Arcetri Astrobiology Laboratory participated in the EURO-CARES, a European Commission H2020 research project, develops a roadmap for a European Sample Curation Facility, to handle samples returned from space exploration missions.

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