

EPSC2018

**SB17/AB3 abstracts**

# Organic Rims on Individual Grains in CP IDPs: Evidence for Organic Formation in the Solar Protoplanetary Disk

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## Abstract

We identified ~100 nm thick organic coatings on individual grains, having a diverse range of mineralogies, in primitive aggregate interplanetary dust particles. These coatings formed after grain condensation from the Solar Protoplanetary Disk, but before aggregation into early Solar System dust particles. This is inconsistent with formation by mineral-specific surface catalysis, but consistent with formation by irradiation and subsequent heating of carbon-bearing ices accreted onto grain surfaces in the cold outer Solar System.

## Introduction

Chondritic porous interplanetary dust particles (CP IDPs) from comets and asteroids, collected by NASA from the Earth's stratosphere, are unequilibrated aggregates of mostly submicron mineral grains. CP IDPs range from ~5 to ~25  $\mu\text{m}$  in size and each has a major element composition roughly similar to CI meteorites ("chondritic"). Most CP IDPs show no evidence of significant post-accretional parent body alteration, which overprints the record of formation processes in meteorites. CP IDPs never experienced significant hydrous or thermal parent body processing, gravitational compaction, or impact shock, and many were minimally heated during atmospheric deceleration. CP IDPs are the most cosmochemically primitive astromaterials available for laboratory study [1], ideal to decipher the record of processes that occurred in Solar Protoplanetary Disk and similar disks around other stars.

### 1.1 Mineralogy of CP IDPs

The equilibrium condensation temperatures of mineral grains in the Solar Protoplanetary Disk were modeled by Lodders [2] using Solar element abundances and a gas pressure representative of 1

AU. No individual mineral in this condensation sequence has chondritic composition, so each CP IDP is an aggregate of minerals formed over a wide temperature range, from 1300 K for silicates to 700 K for sulfides. CP IDPs are dominated by olivines and pyroxenes, with a wide range of Mg/Fe ratios, Fe- and Zn-Fe-sulfides, and glass with embedded metal and sulfides (GEMS), with other minor phases. Grain aggregation must have been inhibited in the formation region, or we would see aggregates of minerals that formed at similar temperatures. A few phases preserve non-solar isotopic ratios, identifying rare pre-Solar grains that survived disk processing.

### 1.2 Organic Grain Coatings

The individual mineral grains in CP IDPs are generally not in direct contact. Transmission Electron Microscope examination shows that many grains are coated by carbonaceous material [3]. X-ray absorption mapping at the C K-edge using a Scanning Transmission X-ray Microscope (STXM) established that the diverse variety of individual grains, including silicates, sulfides, and carbonates, in many CP IDPs are each rimmed with a thin coating of organic matter (Fig. 1 left), ~100 nm thick, independent of the grain composition [4]. X-ray Absorption Near-Edge Structure (XANES) spectroscopy identified both C=C and C=O functional groups in the organic rims [5].

Astronomical observations indicate the vast majority of grains in interstellar space are amorphous [6], so the abundant crystalline grains in CP IDPs must have formed in the Solar Protoplanetary Disk. The organic rims must have been emplaced by processes in the disk after grain condensation, but before aggregation of the grains into dust particles. Organic rims likely aided in aggregation since bare mineral grains stick only in low speed collisions, while organic coatings increase the range of sticking speeds [7].

XANES spectroscopy of organic rims demonstrates the presence of C, N, and O, with N:C and O:C ratios significantly higher than the ratios in meteoritic insoluble organic matter, plotting on the extension of the trend of increasingly primitive organic matter in carbon-bearing meteorites, suggesting these rims are very primitive organic matter (Fig. 1 right) [5].

The silicates in the CP IDPs are believed to have formed in the warm inner region of the Solar Protoplanetary Disk. The size-frequency distributions of the Mg-rich silicates (olivine and pyroxene) and Fe-sulfides show a size-density relationship in different CP IDPs consistent with aerodynamic sorting operating in the disk prior to grain aggregation [8]. This suggests aerodynamic transport of the crystalline mineral grains from the warm inner disk to a region where grains from different formation environments were mixed together.

Our observation that these grain coatings are present on silicates, sulfides, carbonates and GEMS demonstrates that mineral-specific catalysis is not the mechanism of formation. Modeling shows processing by ionizing radiation of ice coated grains in the cold, outer Solar Nebula can produce complex organic molecules [9]. Our identification of organic rims on the surfaces of crystalline mineral grains in the CP IDPs is consistent with this modeling by Ciesla and Sandford [9], providing evidence for the formation of organic matter early in the evolution of the Solar Protoplanetary Disk, after grain formation but before these grains aggregated into dust.

## Summary and Conclusions

In CP IDPs, the best preserved samples of Solar Nebula products, organic coatings forming the contact surfaces between grains implies a three-step

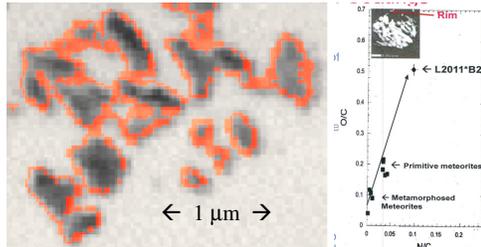


Figure 1: (Left) Absorption image of grains with organic rims in red. (Right) N/C vs. O/C for IDP rim organic, metamorphosed and primitive meteorites.

formation: mineral condensation, emplacement of organic rims, and grain aggregation. These organic rims are the earliest identified organic matter known to have formed in our Solar System. Organic coating of a diversity of minerals is inconsistent with mineral-specific catalysis but consistent with formation by irradiation/heating of carbon-bearing ices that condensed on grain surfaces. Similar processes likely occurred in other protoplanetary disks.

## Acknowledgements

This work was supported by NASA Emerging Worlds grant #NNX17AE59G.

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# Abundance, Enantiomeric, and $^{13}\text{C}$ Isotope Analyses of Meteoritic Aldehydes and Ketones

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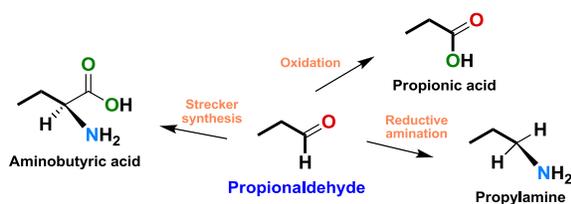
## Abstract

The assessment of the molecular diversity of soluble organic compounds in carbonaceous chondrites provides information about the chemical inventory at the birth of the Solar System and the processes that occurred inside the parent body [1]. Here, we have analyzed the abundance, molecular diversity, and isotopic and enantiomeric compositions of aldehydes and ketones (carbonyl compounds) which may have been precursors for other meteoritic organics.

## 1. Introduction

Central to the study of meteoritic organic compounds is the isolation, identification and quantification of these prebiotic molecules. One of the most thoroughly studied meteoritic organics are aliphatic amino acids; however, even after over 60 years of research, their prebiotic origins remain a major subject of debate [2]. Meteoritic carbonyl compounds may be potential precursors of amino acids, and other compounds such as monocarboxylic acids (MCAs) and amines (Scheme 1). We have assessed the isotopic and enantiomeric composition of meteoritic MCAs and amines [3], [4]; now, we turn our focus to the analyses of carbonyl compounds.

**Scheme 1:** Potential synthetic relationship between aldehydes, ketones, amines and amino acids.



Several aldehydes and ketones have been previously detected from carbonaceous chondrites [5], [6]; however, the methodology used for these analyses hampered the assessment of their isotopic and enantiomeric distributions. We have developed and applied a novel gas chromatography coupled with

mass spectrometry and isotope ratio mass spectrometry method, as well as a workup protocol suited for the simultaneous measurement of the abundance, enantiomeric composition, and compound-specific isotopic analysis of aliphatic short-chained carbonyl compounds ( $\leq 6$  carbons) in CI, CM, CR and CV carbonaceous chondrites.

## 2. Results and Discussion

The total concentrations of aldehydes and ketones we found are shown in Figure 1. We measured total abundances of aldehydes that were higher than that of ketones; with acetaldehyde and formaldehyde being the most abundant aldehydes, and acetone the most abundant ketone across different carbonaceous chondrites. The total concentrations of carbonyl compounds among CI and CM chondrites ranged within similar values, while those in CR chondrites seemed to be more dependent on the levels of aqueous alteration occurred in the parent body. We observed higher concentrations of formaldehyde over acetaldehyde in the low aqueously altered CM and CR chondrites (EET 96029, LAP 02342, GRA 95229, and MIL 09657). These collective data support the theory that parent body processes in addition to the yet-to-be known organic-precursor budget of carbonaceous chondrites, play an important role in the abundance and molecular distribution of soluble meteoritic organics.

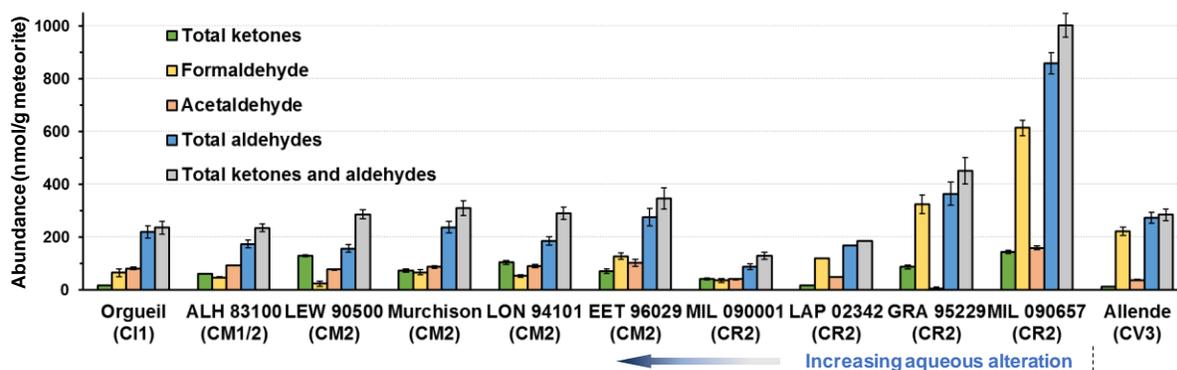
We observed racemic compositions of the chiral 3-methyl-2-pentanone and 3-methylpentanal; these results are consistent with racemic compositions found for meteoritic aliphatic MCAs and amines [7], [4]. The racemic compositions of the carbonyl compound suggest that these compounds were either racemic prior to their accretion inside the parent body, or that after accretion, aqueous processes racemized them or resulted in enhancements of any initial symmetric imbalance that are below our current detection limits.

The varying concentrations and unique molecular diversity, plus the racemic composition of carbonyl compounds in meteorites with distinct levels of

parent body processing, support an extraterrestrial origin for these compounds. However, we interpreted that the carbonyl compounds found in Allende (CV3) are product of terrestrial contamination based on the  $^{13}\text{C}$ -depleted values measured and the high concentrations of biological MCAs we found in a previous analysis of the same material. The carbon isotope ( $\delta^{13}\text{C}$ ) compositions of carbonyl compounds contrast with the  $\delta^{13}\text{C}$  values previously reported for amino acids and amines [8], [4], but they fall within the  $\delta^{13}\text{C}$  range of MCAs [3].

### 3. Conclusions

Aliphatic aldehydes are more abundant than ketones in the samples we investigated. The combined concentrations of both compound classes resulted similar in CI and CM chondrites, but more aqueous processing-dependent in CR chondrites. We observed higher abundances of acetaldehyde over formaldehyde in more aqueously altered meteorites. We detected racemic compositions of carbonyl compounds and  $\delta^{13}\text{C}$  values that are within the range of MCAs. Future efforts aimed to unveil the complex synthetic relationship between various meteoritic organics are needed to implement constraints on their meteoritic origin.



**Figure 1:** Abundance of carbonyl compounds in CI, CM, CR and CV meteorites. Meteorite groups are arranged according to their aqueous and thermal alteration.

### Acknowledgements

This research was supported by NASA's Emerging Worlds Program (award 14-EW14\_2-0010 to J.E.E. and J.C.A.), the NASA Astrobiology Institute and the Goddard Center for Astrobiology, and a grant from the Simons Foundation (SCOL award 302497 to J.P.D.).

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# Photo- and thermo-chemistry of ices as a source for organic matter: from astrochemistry to astrobiology

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## Abstract

Extraterrestrial ices are abundant in astrophysical environments linked to star forming regions as well as environments where protoplanetary disks, planets and various debris such as comets and asteroids do form. These ices can be easily simulated in the laboratory, leading to the formation of organic residues that can be analysed by classical gas analytical chemistry methods. Among detected species, many amino-acids are observed. Interestingly aldehydes and sugars were also detected. Over-irradiation of the residues under vacuum likely produces an insoluble organic material that resembles the one observed in primitive meteorites. Astrobiological implications from astrochemistry may thus be seriously considered.

## 1. Introduction

The abundance and importance of ices in astronomical settings cannot be understated. Ices are observed in the infrared spectra of protostars at the end phase of molecular clouds lifetime prior to the formation of protoplanetary disks. In these disks, many objects do contain dirty ices such as comets, asteroids and icy moons of giant planets in our Solar System. Simulating these ices in the laboratory is a not so difficult task with the use of matrix isolation techniques [1] in which gas phase simple molecules are deposited onto a cold infrared transparent window. Various methods to impart energy within these ices do exist, pertaining to different environments in space. In our case, following the model given by [2], we use essentially Lyman  $\alpha$  photons provided by a plasma discharge microwave lamp.

## 2. Organic matter from ices

### 2.1 The formation of organic residues

The sample, a gas mixture of abundant interstellar molecules ( $H_2O$ ,  $CH_3OH$ ,  $NH_3$  in our case) is deposited under vacuum on a  $MgF_2$  window, cooled to 77 K and simultaneously photolyzed with the UV discharge lamp to ensure for a complete penetration of the sample with UV photons. In most of our experiments we use around 1 to 10 Ly $\alpha$  photons per deposited molecules. At the end of this phase, the sample is warmed-up to room temperature where the presence of a semi-refractory organic residue is always observed in the infrared spectrum of the window as well as visually (see Figure 1). Many examples of these residues can be found in [3]. We assume that such a residue does represent an analogue of the Soluble Organic Matter (SOM) present in primitive meteorites.

### 1.1 Targeted molecules in the residue

About 100  $\mu g$  (up to 300  $\mu g$ ) is obtained at each run which renders the analytical procedure quite elaborate. In the group of Uwe Meierhenrich in Nice, the use of a performing double dimensional gas chromatographic apparatus (GCxGC-TOFMS) has proven its efficiency for such a task. This targeted technique is very sensitive and we ensure that any contamination from the analytical procedure is avoided by using  $^{13}C$  isotopic labelling in the  $CH_3OH$  from the initial gas mixture. Targeted searches for amino acids have been performed and have shown many amino acids, including proteigeneous ones to be present in the sample as well as some diamino acids. A complete list of those can be found in [5]. Second, the search for sugars have been also performed in similar samples with a different

extraction protocol. They have revealed the presence of 8 aldehydes including glycolaldehyde and, most importantly, glyceraldehyde, the first sugar of the ose family [6]. Later on, using the same techniques with a more elaborated protocol to make sure that all the sugars could be detected, a suite of sugars was found, including ribose, a most important component of the RNA molecule since it is part of the backbone of this RNA [7]. A key figure of these results is the quite large abundance of sugars such as ribose with the presence of various aldopentoses (5 carbon atoms) which is tentatively explained as due to a reaction within the evaporation of the ice that polymerizes  $H_2CO$  and produces all these sugars via a reaction in part similar to the well-known formose reaction.

## 2.2 Insoluble organic materials

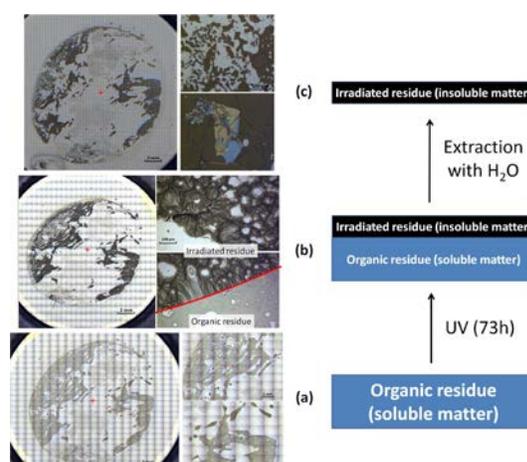
We decided to post irradiate the residue at room temperature (300 K) in vacuum. Actually this experiment was serendipitously performed while testing the irradiation of residues with UV-Circularly Polarized Light in order to obtain a symmetry breaking in the amino acids detected (L vs D amino acids). This experiment is described in [8] with its astrophysical explanation for the origin of amino acid enantiomeric excesses in meteorites. Unexpectedly to us, after extracting the SOM part of the sample, some insoluble part was indeed remaining. This was confirmed by a following experiment where high UV irradiation doses were delivered to the sample (10 keV per bond). Indeed the sample starts to “aromatize” and passes through a stage where it resembles the well-known IOM from primitive carbonaceous chondritic meteorites. This is briefly depicted in Figure 2 taken from [9].

## 3. Conclusions

UV irradiation of ices does provide organic materials that we assume to be analogues of the soluble organic materials in primitive meteorites. Their importance to possibly feed prebiotic chemistry on telluric planets must be seriously considered. This approach must follow a holistic astrophysical scenario which depicts the global astrochemical evolution of our Galaxy [10]. However further experiments in preparation will consider the evolution of this material under specific environmental conditions, adapted to early Earth, in order to test far from equilibrium processes that are necessary to establish the inert to living transition in an organic molecular network in interaction with a specific environment, a minimal definition for “life”.



**Figure 1:** an image of the residue under visible light obtained with a microscope (X60)



**Figure 2:** Transformation of laboratory SOM to laboratory IOM upon over irradiation [9].

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# From Astrochemistry to Prebiotic Chemistry: the Organic Matter Evolution

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## Abstract

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

## 1. Introduction

A living organism arranges a set of chemical processes to maintain a non-equilibrium state by exchanging matter and energy with its environment, as well as to reproduce and evolve. A large set of molecules and a given environment therefore interact to sustain a living organism. The living cannot exist and grow without chemical processes, whereas a chemical reaction can take place without the necessity of living. Chemistry can be considered as "universal." However, clues that the emergence of life is a common and inevitable phenomenon in our Galaxy have not yet been provided. Currently, the known life forms resides only on the Earth. To determine if other planetary systems could undergo a similar evolution, it seems important to trace the fate of organic matter. This will help to understand what chemical processes could be established, in which environments and from which sources of matter and energy <sup>[1]</sup>. The knowledge of this chemical evolution will provide clues about the possibility of finding

other environments that may lead to the emergence of biosystems.

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

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

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

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

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

### 4. Conclusion

The studies on the chemical evolution in astrophysical environments have demonstrated that organic matter is formed abiotically, destroyed and available everywhere in the Universe, in more or less complex forms. Carbon, hydrogen, nitrogen and oxygen tend to develop spontaneously a chemistry

that is universal and not limited to the biochemistry of living organisms. However, the presence of organic matter in various astrophysical environments is not sufficient for the emergence of life. Only astrophysical environments presenting a specific set of physical and chemical conditions enabling the development of far-from-equilibrium processes will enable the self-organisation of organic matter towards the living state. For understanding where life can arise, we have to understand which environments could gather these conditions.

### Acknowledgements

This work has been funded by the French national programme "Physique Chimie du Milieu Interstellaire" (P.C.M.I, INSU), "Programme National de Planétologie" (PNP, INSU), the "Centre National d'Études Spatiales" (C.N.E.S) from its exobiology program, funding from the French Agency of National Research (ANR) through RAHIA, VAHIA and PetiSystems programs.

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# The search for polyynes in electron irradiated ices of astrochemical relevance

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## Abstract

We present new experimental results on the formation of polyynes by 1 keV electron irradiation of simple hydrocarbons and their mixtures with  $N_2$  and  $H_2O$  under conditions that mimic the physical conditions on the grains in the dense molecular clouds in the interstellar medium (ISM) and the surfaces of small bodies and icy satellites in our Solar System.

## 1. Introduction

It is well known that polyynes ( $H(-C \equiv C)_nH$ ) are ubiquitous in the interstellar medium (e.g. Jolly and Benilan, 2008 and references therein). Recent astrochemical models suggest that they are formed in the solid state and then released in the gas phase by thermal and/or non-thermal processes. Compagnini et al. (2009) showed the laboratory formation of polyynes by means of Raman spectroscopy through the energetic ion bombardment of solid acetylene; while Cuyllé et al. (2014) detected newly formed polyynes in the VUV spectral range after irradiation of acetylene ice (and its mixture with water) with UV-photons.

## 2. Experimental

Here we present new experimental results on the formation of polyynes by 1 keV electron irradiation of simple hydrocarbons and their mixtures with  $N_2$  and  $H_2O$  under conditions that mimic the physical conditions on the grains in the dense molecular clouds in the interstellar medium (ISM) and the surfaces of small bodies and icy satellites in our Solar System. As discussed in Cuyllé et al. (2014), a spectral range particularly suited for the detection of

single polyynes and cyano-polyynes (i.e., with a specific number of carbon atoms in a linear chain) is the VUV spectral range, i.e. 120-340 nm. On the other hand, the more commonly used mid-IR spectral range by means of FTIR spectroscopy ( $4000-600\text{ cm}^{-1}$ ) is better suited for the identification of simple single molecules and functional groups of larger species (e.g., polyynes, cyano-polyynes and the refractory organic materials formed after energetic processing of hydrocarbons). Therefore, our experiments are performed using the Open University (OU) portable high-vacuum apparatus in two different locations (i.e., the synchrotron ASTRID2 facility – ISA, Aarhus University in Denmark and the Astrochemistry laboratory at the OU in the UK) to extend the accessible spectral range from the VUV (120-340 nm) to the mid-IR ( $4000-800\text{ cm}^{-1}$ ), respectively.

## 3. Results

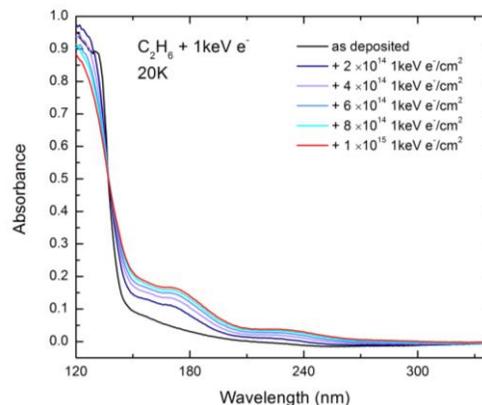


Figure 1: Irradiation of ethane ( $C_2H_6$ ) with 1keV electrons at different fluencies.

## Acknowledgements

The research leading to these results has received funding from the project CALIPSOplus under the Grant Agreement 730872 from the EU Framework Programme for Research and Innovation HORIZON 2020. The research of Z.K. was supported by VEGA – the Slovak Grant Agency for Science (grant No. 2/0023/18), COST Action TD 1308 and COST Action CM 1401.

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# Profiling meteorite soluble organic matter using (ultra)high resolution organic spectroscopy

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## Abstract

We present here a review of the state of the art in non-targeted high resolution analysis of the soluble organic fraction of various meteorites; these include carbonaceous chondrites as well as achondrites and ordinary chondrites.

## 1. Introduction

Understanding the origin and evolution of organic matter, is linked to observationally-derived astrochemistry (telescopic observations) and the laboratory wet chemical analysis of return objects and meteorites. The molecular composition and diversity of non-terrestrial organic matter in carbonaceous chondrites was studied by means of both, targeted [1] and non-targeted [2,3] chemical analytical approaches, leading to new insights. Targeted chemical analyses are hypothesis-driven and are largely focused on molecules of biological/prebiotic interest. In a non-targeted approach, all analytes are globally profiled within the analytical possibilities without biased or constrained hypothesis in order to gain comprehensive information. We review in this presentation the state of the art in using non-targeted high resolution organic spectroscopy.

## 2. The analytical approaches

Ultrahigh-resolving analytics, like high field Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) and nuclear magnetic resonance spectroscopy (NMR), represent a powerful tool to allow insights into the holistic complex compositional space to tens of thousands of different molecular compositions and functional groups and likely millions of diverse structures. This could be observed in solvent extracts of pristine carbonaceous

meteorites [2, 3], and suggests that interstellar chemistry is extremely active and rich. Since then we studied the chemical composition of thousands of individual components out of complex organic mixtures, as accessed in the solvent-accessible organic fraction, extracted under mild conditions, from diversely-classified and heated meteorites

## 3. Results

We described that heteroatomic organic molecules play an important role in the description of non-terrestrial chemical evolution. The thermally and shock-stressed Chelyabinsk (LL5) [4] showed high number of nitrogen counts within CHNO molecular formulas, especially in the melt region. This match of the organic molecular profile with the petrologic character could be also observed for Novato (L6) [5], Braunschweig (L6) and the latest German fall Stubenberg (LL6) [6]. Additionally, the extremely thermally altered Sutter's mill (C-type) [7] reflects a loss in the organic diversity, but an increase in the polysulphur domain, as compared to other CM2-analyzed falls. The increase of polynitrogen and polysulphur compounds could be simulated in laboratory experiments by heating Murchison (CM2). Recently we reported the discovery of a previously unrecognized chemical class, dihydroxymagnesium carboxylates,  $[(HO)_2MgO_2CR]^-$ , gained from nonterrestrial meteoritic analyses [8]. These thermostable compounds might have contributed to the stabilization of organic molecules on a geological time scale, which emphasizes their potential astrobiological relevance.

The resulted extreme richness in chemical diversity offers information on the meteoritic parent body history and help in expanding our knowledge or astrochemistry towards higher molecular masses and complex molecular structures.

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# Organic matter and exogenous hypothesis

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## Abstract

The idea of an exogenous origin of prebiotic species taking part in the construction of living organisms relies on a delivery of these species by meteorites and comets in-falls on the Earth. On another side real complex prebiotic molecules are not detected in the interstellar medium (ISM). Here we consider three fundamental points: i) the possible detection of small peptides, ii) the role of environmental conditions on amino acids, iii) the possible survival of these species to the radiation field.

## 1. Introduction

The fact that ~90% of the simple molecules identified [1] are the most stable isomers of their respective families is consistent with what is called the minimum energy principle (MEP) [2]. Using MEP as a pragmatic tool, we look for new candidates in the peptide family that is known to be a precursor of the more complex proteins and metabolites like urea. Using the same tool we look at amino acids Glycine (Gly) and Alanine (Ala) and find that they are not the most stable compounds in neutral form but are the most stable as protonated or zwitterions [3]. Here we consider whether the relative abundances of isomers could help in the characterization of the environment in which they are formed. The most primitive meteorites provide a window on organic matter in the solar system. In this geo-mineralogical context parent bodies appear as spatial laboratories in which aqueous alteration may have created the conditions of a rich catalytic chemistry in presence of metallic elements. After completion of a cooling process (solidification of the ice ~ 150K), the organic matter, embedded in the matrix of the carbonaceous chondrites, may be delivered to the Earth. In this scenario the role of these meteorites would be limited to that of means of communication.

## 2. Peptide models

A first study shows that the peptide bonding -CO-N-

is most probably more common than originally thought. Formamide H-CO-NH<sub>2</sub> is the lowest energy isomer of the generic formula CH<sub>3</sub>NO. Up to now, it is the only isomer detected (1971) in the ISM [1]. After detection (2006) of CH<sub>3</sub>CONH<sub>2</sub> [1], the next member of the amide series CH<sub>3</sub>NHCHO [1] has been identified (2017) in agreement with MEP. The stability of the -[N-CO]- arrangement has been confirmed by the detection of Urea, and Thiourea should also be identified [4].

## 3. Amino acids and environment

According to the environment the most stable isomer is not the same. Neutral or protonated in gas phase, protonated or zwitterionic as a result of an aqueous alteration: the relative abundances appear as tracers of the geochemical structure of the parent bodies at the origin of the carbonaceous chondrites.

Table 1: Relative energy of amino acids isomers

C2H5NO2	ΔE	C2H7NO2	ΔE
Neutral isomers			
CH <sub>3</sub> NHCOOH	0.0	CH <sub>3</sub> CH <sub>2</sub> NHCOOH	0.0
CH <sub>3</sub> OC(NH <sub>2</sub> )O	4.7	CH <sub>3</sub> CH <sub>2</sub> OC(NH <sub>2</sub> )O	3.3
NH <sub>2</sub> CH <sub>2</sub> COOH	10.3	(CH <sub>3</sub> ) <sub>2</sub> NCOOH	7.0
HOCH <sub>2</sub> C(NH <sub>2</sub> )O	10.6	HOCH(CH <sub>3</sub> )CONH <sub>2</sub>	10.3
HOCH <sub>2</sub> NHCHO	17.0	CH <sub>3</sub> -OOC-NH-CH <sub>3</sub>	10.6
		NH <sub>2</sub> CH(CH <sub>3</sub> )COOH	10.8
		NH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> COOH	11.5
Protonated isomers			
NH <sub>3</sub> <sup>+</sup> -CH <sub>2</sub> COOH	0.0	NH <sub>3</sub> <sup>+</sup> CH <sub>2</sub> CH <sub>2</sub> COOH	0.0
CH <sub>3</sub> -NH-C(OH) <sub>2</sub> <sup>+</sup>	2.2	NH <sub>3</sub> <sup>+</sup> CH(CH <sub>3</sub> )COOH	5.8
CH <sub>3</sub> -OC(OH <sup>+</sup> )NH <sub>2</sub>	4.7	HOCH <sub>2</sub> CH <sub>2</sub> C(OH <sup>+</sup> )NH <sub>2</sub>	6.5
HO-CH <sub>2</sub> C(OH <sup>+</sup> )NH <sub>2</sub>	6.0	CH <sub>3</sub> CH <sub>2</sub> OC(OH <sup>+</sup> )NH <sub>2</sub>	9.5
NH <sub>3</sub> <sup>+</sup> -CH <sub>2</sub> O-CHO	15.4	CH <sub>3</sub> CH <sub>2</sub> NHC(OH) <sub>2</sub> <sup>+</sup>	9.6
Zwitterion isomers <sup>(*)</sup>			
NH <sub>3</sub> <sup>+</sup> -CH <sub>2</sub> COO <sup>-</sup>	0.0	NH <sub>3</sub> <sup>+</sup> CH(CH <sub>3</sub> )COO <sup>-</sup>	0.0
CH <sub>3</sub> -NH <sub>2</sub> <sup>+</sup> -COO <sup>-</sup>	2.6	NH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> COO <sup>-</sup>	0.5
		CH <sub>3</sub> CH <sub>2</sub> -NH <sub>2</sub> <sup>+</sup> -COO <sup>-</sup>	3.7

*Technical note:* Density functional theory (DFT), within the B3LYP/6-311G\*\* formalism was used throughout, except for zwitterions<sup>(\*)</sup> where dispersion effects are introduced at the MP2 level. All structures, fully optimized, were verified to be stationary points by vibrational analysis. ΔE(kcal/mol.)

Based on MEP, the quantum simulations show that Gly,  $\alpha$ - and  $\beta$ -Ala isomers are the most stable species in only two conditions, namely in protonated or in zwitterionic forms. However, it is remarkable that the stability order for Ala is not the same in both cases. In a protic environment,  $\beta$ -alanine is more stable than the biological  $\alpha$  isomer and for that reason should be more abundant. It is what is found in the most extensively parent-body altered chondrites Orgueil, Ivuna and Essebi. In a neutral water environment, that favors the zwitterionic structures,  $\alpha$ -alanine is more stable than the  $\beta$ -isomer and for the same energetic reason should be more abundant. It is precisely what is found in meteorites that have experienced terrestrial weathering.

## 4. Survival of amino acids

It has been shown that several amino acids can be formed in the laboratory by UV irradiation of interstellar ice analogues containing H<sub>2</sub>O, CH<sub>3</sub>OH, NH<sub>3</sub>, CO, and CO<sub>2</sub> [5]. The survival of these amino acids embedded in the ice along their journey to the Earth is still an open question.

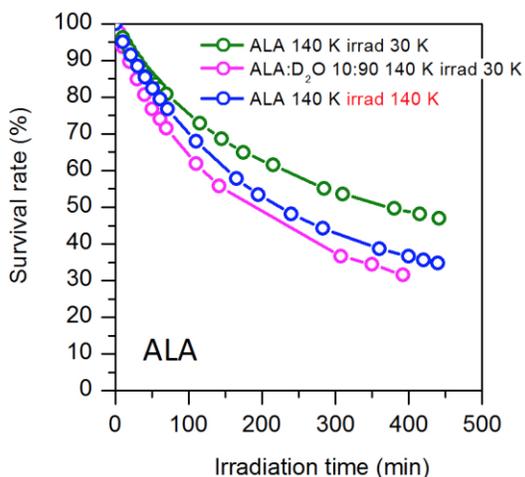


Figure 1: Ala survival followed by  $\nu$  CO frequency.

Irradiation in ultra high vacuum (30K) on the TEMPO beam line (SOLEIL synchrotron), simultaneously with near-edge X-ray absorption spectroscopy was carried out. The experiments show that Ala, like Gly [6] is only partially destroyed. Its abundance is found to stay at a level of  $\sim$  30-40% of the initial concentration, for an irradiation dose equivalent to three years of solar radiation (at a distance of one astronomical unit).

This result supports the hypothesis that, if trapped in icy environments and/or in the interior of interplanetary particles and meteorites, amino acids may partly resist the radiation field to which they are submitted and survive the journey to the Earth.

## 5. Summary and Conclusions

Using MEP as a pragmatic tool, we show that the peptide link -CO-NH- is the most stable arrangement leading to amides and to urea and by extension to peptides. These simulations, which agree with observations and experiments can be extended to new targets to search for in the ISM. Looking at amino acids Glycine and Alanine we find that they are not the most stable compounds in neutral form but are the most stable as protonated or zwitterions. The relative abundances of isomers differ with the nature (protonated or zwitterions) and represent a possible tracer of the environment in the parent bodies where they are formed. Partial survival of these acids when embedded in the ice has been demonstrated.

However, one critical question remains unsettled, i.e. whether homochirality is preserved in these transfer conditions. It is currently under investigation.

## Acknowledgements

This work was supported by CNRS national programs PCMI (Physics and Chemistry of the Interstellar Medium), EPOV (Environment of Planets and Origins of Life) and COST Action CM0805 (The Chemical Cosmos).

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## H/C elemental ratios of the refractory organic matter in cometary particles of 67P/Churyumov-Gerasimenko

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### Abstract

For two years, the time-of-flight secondary ion mass spectrometer COSIMA (COmetary Secondary Ion Mass Analyzer), on board the Rosetta orbiter, performed *in situ* analyses of the dust particles ejected from the comet 67P/Churyumov-Gerasimenko (hereafter 67P) [6, 7]. Exploiting different analyses of organic analogs that have been analyzed via the COSIMA reference model, we are now able to estimate the H/C elemental ratio of the 67P cometary particles.

### Introduction

The Rosetta mission was dedicated to the study of the comet 67P. Between September 2014 and June 2016, more than 35,000 particles and particle fragments were collected [9] and, among them, around 250 were analyzed by the COSIMA mass spectrometer in positive and negative secondary ion registration modes. Here we are interested in the chemical composition of ejected cometary particles originating from the nucleus. Cometary organic matter, including solid organic matter in the particles, was poorly characterized by *in situ* observations before the arrival of Rosetta at the vicinity of the 67P nucleus. Using mass spectra obtained by the COSIMA instrument, we have shown that this solid cometary organic matter was different from all the well characterized organic compounds analyzed during the calibration phase on ground (such as carboxylic acids, amino acid, nucleobases, hydrocarbons and PAHs) [5, 8]. On the other hand, similarities with

Insoluble Organic Matter (IOM) extracted from carbonaceous chondrites are notable [5]. Thus, the 67P cometary particles contain a high molecular weight organic matter. Moreover, we have shown that the cometary particles are among the most carbon-rich objects in the Solar System, containing about 50% by mass of organic matter [4]. Through analyses of different complex carbonaceous samples (including sedimentary rocks and IOMs) with the ground reference model of COSIMA, we attempted to establish correlations between ionic ratios and H/C elemental ratios in order to estimate the H/C elemental ratios in the 67P cometary particles.

### Method

Numerous carbonaceous samples, with H/C elemental ratios ranging from 0 to 2.1 [1, 2, 3, 10], have been recently analyzed with the reference model of COSIMA. They are used to construct calibration curves involving measured ionic ratios and H/C elemental ratio. The hydrogen of 67P particles is thought to be mainly contained in the organic phase since COSIMA mass spectra do not show signatures from hydrated minerals [4]. Thus, the estimated cometary H/C is related to the organic component. Several ionic ratios, such as  $C_2H^-/C_2^-$  and  $H^+/C^+$ , were tested in the search for calibration lines (e.g., Figure 1). Then, the H/C elemental ratio have been estimated for two sets of about 20 particles, based on the measured ionic ratios and calibration curves.

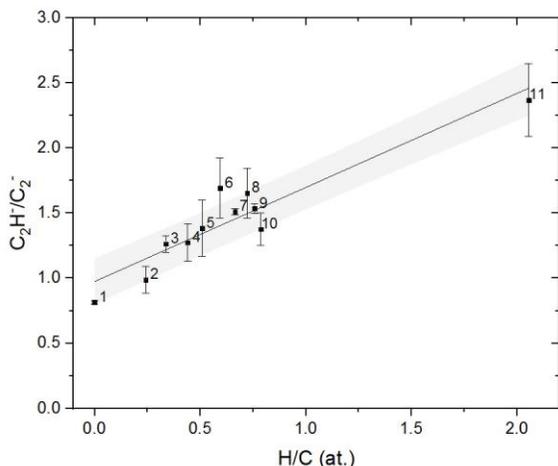


Figure 1: Example of H/C calibration curve, using the  $C_2H^-/C_2^-$  ionic ratio measured from negative ion mass spectra. The black squares are the different calibration samples: (1) Graphite, (2) IOM PCA, (3) IOM Tagish Lake original, (4) IOM Tagish Lake 11v, (5) IOM Tagish Lake 11i, (6) IOM Tagish Lake 11h, (7) IOM GRO 95566, (8) IOM Tagish Lake 5b, (9) IOM EET 92042, (10) IOM GRO 95577, (11) Hexatriacontane. The individual error bars are the uncertainties on the ionic ratio. The grey area represents the  $1\sigma$  uncertainty.

## Results and conclusions

The analyses of the carbonaceous samples show that the H/C elemental ratio correlates with several ionic ratios (especially  $C_2H^-/C_2^-$  and  $H^+/C^+$ ). Using these calibration lines, H/C elemental ratio can be estimated for numerous cometary particles. The cometary H/C elemental ratio suggests values equal or higher than the one measured in the IOMs (the highest H/C in IOM being 0.8 [1]). Considering that the cometary hydrogen is mainly present in the organic phase and mostly linked to carbon [4], these results imply that the refractory macromolecular organic matter detected in 67P dust particles might be less unsaturated than the one in meteorites.

## Acknowledgements

COSIMA was built by a consortium led by the Max-Planck-Institut für Extraterrestrische Physik, Garching, Germany, in collaboration with: the Laboratoire de Physique et Chimie de l'Environnement et de l'Espace, Orléans, France; the Institut d'Astrophysique Spatiale, CNRS/Université Paris Sud, Orsay, France; the Finnish Meteorological

Institute, Helsinki, Finland; the Universität Wuppertal, Wuppertal, Germany; von Hoerner und Sulger GmbH, Schwetzingen, Germany; the Universität der Bundeswehr, Neubiberg, Germany; the Institut für Physik, Forschungszentrum Seibersdorf, Seibersdorf, Austria; and the Institut für Weltraumforschung, Österreichische Akademie der Wissenschaften, Graz, Austria; and is led by the Max-Planck-Institut für Sonnensystemforschung, Göttingen, Germany. We acknowledge the support of the national funding agencies of Germany (DLR, grant 50 QP 1302), France (CNES), Austria, Finland and the ESA Technical Directorate. Rosetta is an ESA mission with contributions from its Member States and NASA. R.I. acknowledges support from the Labex Exploration Spatiale des Environnements Planétaires (ESEP; no. 2011-LABX-030).

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# D/H and microstructure of irradiated organic dust analogs

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## Abstract

It is unknown how the widespread organic matter in primitive Solar System materials formed. In this study, we explore UV and X-ray irradiation as drivers in the formation of organics from simple ices. We compare microstructures and H isotopic compositions of samples produced under controlled irradiation experiments simulating environments in dense molecular clouds or the outer Solar Nebula with those of natural samples. The irradiation results in an increase of  $\delta D$  of up to  $\sim 1000\%$  and the induction of some graphitic ordering at the molecular level.

## 1. Introduction

Organic matter is present in a wide range of primitive Solar System materials, and how it formed is a matter of debate [1]. Organic matter in primitive meteorites has much higher D/H and  $^{15}\text{N}/^{14}\text{N}$  ratios than the Sun, and the process that formed organic matter likely contributed to these heavy isotopic compositions [1]. In this project, we evaluate irradiation of ices as a formation pathway for organic matter by comparing the H mass fractionation resulting from these processes with the H isotopic compositions of natural samples. In addition, we investigate the microstructure of the samples using scanning transmission electron microscopy (STEM).

Relatively complex organic molecules can be made in the laboratory by UV irradiation of simple ices under vacuum at temperatures of  $\sim 10\text{--}15$  K. These ices are believed to be present in molecular clouds and the outer Solar Nebula. UV irradiation breaks chemical bonds and forms reactive ions and radicals which will recombine upon warm-up to form more complex molecules. Organic materials that formed from ices in this manner may have been irradiated

further in the Solar Nebula, resulting in the alteration of their structure, chemical composition, and/or isotopic composition [2,3]. Electron irradiation of organic matter (epoxy, cyanoacrylate, terrestrial kerogens, and polymers) can induce D-enrichments of  $\delta D$  up to  $\sim 1000\%$  [2,4]. UV irradiation results in similar D enrichments [4]. Consequently, it appears that the type of irradiation resulting in changes in H isotopic composition is not as important as the total energy deposited into the organics [4]. In this study, we investigate the microstructure and D/H ratios of organics produced from astrophysical ice analogs of different compositions, and how these D/H ratios vary when these organics are irradiated with different energies and doses of X-ray photons.

## 2. Methods

Samples were produced at the Astrochemistry Laboratory of NASA Ames following the methods in [5]. Four different starting ice mixtures were used:  $\text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{CO}:\text{NH}_3 = 100:50:10:10$  (B22, B18), and  $100:50:20:10$  (C3),  $\text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{CO}:\text{NH}_3:\text{C}_{10}\text{H}_8 = 100:50:10:10:1$  (B21, B23, B19) and  $100:50:20:10:1$  (C5). The most significant difference between the samples is that some contain naphthalene ( $\text{C}_{10}\text{H}_8$ ) and some do not. The recovered samples were further irradiated with X-rays with different energies, broad band (80-450 eV) or C edge (293 eV), and durations at room temperature (RT) and under vacuum at the National Synchrotron Radiation Research Center (NSRRC) in Taiwan.

Irradiated and un-irradiated fractions of the samples were analyzed for H isotopic compositions using the Carnegie Cameca NanoSIMS 50L. For each sample, at least five particles were analyzed. Data is presented as permil deviations relative to SMOW (Fig.1). Some samples were also analyzed with the Nion UltraSTEM 200-X at NRL, Washington DC.

Annular dark field images and electron energy loss spectra were collected at 60 kV to assess structures and C bonding.

### 3. Results

The samples that were analyzed using STEM all appeared amorphous in the images. Electron energy loss (EELS) spectra indicate that the RT post-irradiation induces some degree of graphitic ordering on a molecular scale in all samples, but there were no indications of crystalline graphite. There are no obvious variations in the degree of graphitization with radiation energy or dose in the samples analyzed so far.

All X-ray irradiated samples were enriched in D compared to SMOW (Fig. 1). In the samples without naphthalene, enrichment of D relative to H appears to have occurred already during the formation of organics from ices under UV light, with  $\delta D$  between ~500 ‰ and 1200 ‰ (Fig. 1). The equivalent, not post-irradiated samples with naphthalene tend not to be enriched in D. Instead, D enrichment in the samples with naphthalene tends to occur during X-ray irradiation, probably due to the loss of H atoms as bonds break [4].  $\delta D$  in the samples without naphthalene appears to decrease with increasing photon dose. This is harder to understand and indicates that processes induced by irradiation of these samples are more complex than previously thought.

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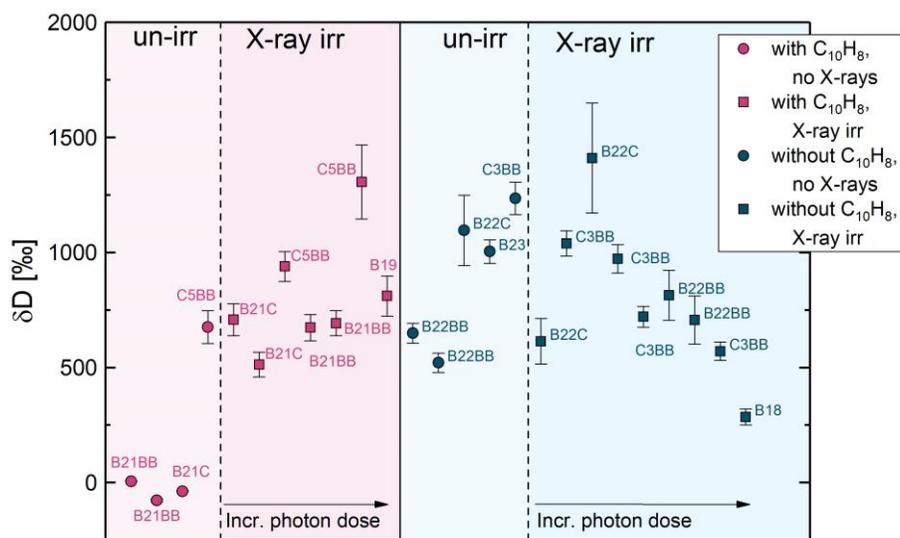


Figure 1.  $\delta D$  of the samples analyzed so far. The samples are divided into two groups: with (pink) and without (blue) naphthalene. The samples are ordered relatively to the increasing photon dose, but the photon dose is not to scale.

## UV luminescence characterisation of organics in Mars-analogue substrates

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### Abstract

Detection of organic matter is one of the core objectives of future Mars exploration. Detection of organic signatures are often hampered or modified by interaction with the host geological substrate. In that respect, UV excited Photoluminescence imaging offers a contactless, non-destructive and, through the addition of imaging, spatially resolved tool. We conducted UV induced photoluminescence analyses of (i) Mars analogue sediments and synthetic salts doped with polyaromatic hydrocarbons (PAHs), and (ii) CM carbonaceous chondrites and terrestrial kerogen. We show that that detection of PAHs in inorganic substrates is possible within gypsum and halite. Iron oxide, ubiquitously present on Mars' surface, hampers but does not completely quench the UV luminescence emission. Finally, the maturity of organic carbonaceous material influences the luminescence response.

### 1. Introduction

Delivery of exogenic organic matter is a daily process on Mars, up to  $4 \times 10^{-4} \text{ g. m}^{-2} \text{ yr}^{-1}$  [1]. A fraction of this matter comprises PAHs, that are both ubiquitous in space and of astrobiological interest [2, 3]. The study of the fate of PAHs is the first step towards the detection of organic matter and putative organic biosignatures in situ on the martian surface. UV luminescence offers a new technique to achieve this [4, 5], whereby UV photon interactions cause electronic transitions to higher-energy states, followed by a quick relaxation and emission of a photon of longer wavelength – generally in the visible range. Compared to Raman, UV luminescence is several orders of magnitude more sensitive than Raman [6], while Raman provides more detailed structural information. Recently, the Scanning Habitable Environments with Raman & Luminescence for Organics & Chemicals (“SHERLOC”) instrument was selected as part of the payload for the NASA Mars 2020 Rover mission. This instrument is a deep UV ( $\lambda_{\text{ex}}=248.6 \text{ nm}$ ) Raman and Luminescence imaging spectrometer [7], and will be the first dedicated spectrometer with UV capability to

be deployed at the Martian surface. Here we test the potential of UV photoluminescence for detection of (i) low concentration PAHs embedded in Mars synthetic and natural analogues, and (ii) organic matter present in CM carbonaceous chondrites as a proxy for organics delivered to the Martian surface.

### 2. Methods and samples

Three Mars analogue sediments from Iceland were selected to represent the three broad mineral epochs of Mars: Mudstone (phyllosilicate), Gypsum (sulfate) and a Fe-oxyhydroxite “Oxide” sediment (iron oxide). These were spiked with either anthracene or pyrene (15 ppm, Sigma Aldrich PAHs solutions) and then pressed into pellets. Synthetic epsomite and halite crystals were prepared from  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , and NaCl saturated solutions, including solutions spiked with either anthracene or Perylene (2 ppm), and solutions additionally spiked with iron oxide (hematite, 1 w. %). Finally, three CM chondrites were analysed, including the Meteorite Hills MET01072 meteorite (CM 2.3, 0.49 g) and the Alan Hills meteorite ALH84044 (CM2, 1.045 g), loaned from NASA JSC, USA, and Murchison (CM2.5, 1 g) loaned from the Natural History Museum, UK. A kerogen type IV sample was also included. UV luminescence analyses were performed both at room temperature, and at low temperature (30K) using the Hyperspectral Luminescence and Optical Spectroscopy (HeLIOS, Cross et al. 2013), with a number of excitation wavelengths ( $\lambda_{\text{ex}}$ ) ranging from 225 – 375 nm.

### 3. Results and Discussion

**Sediments**-Differences in actual luminescence response are visible for Gypsum at  $\lambda_{\text{ex}} = 280 \text{ nm}$  (figure 1-A, D) in the addition of perylene and anthracene, resulting in an increased luminescence at ~ 420 and 500 nm (Figure 1A). With  $\lambda_{\text{ex}} = 365 \text{ nm}$ , perylene does not produce such a large response when spiked onto gypsum. When spiked with PAHs, the Mudstone luminescence response shows only minimal changes with  $\lambda_{\text{ex}} = 280 \text{ nm}$  excitation at ~420 nm and 580 nm (Figure 1B). PAHs on the Oxide matrix have little to no effect (Figure 1C and F). Thus, as previously observed for pure PAHs [8], the maximum

wavelength intensity for 2-5 rings PAHs is located at  $\sim 420$  nm. **Salts**-The addition of PAHs influences the luminescence response only at  $\lambda_{\text{ex}} = 365$  nm (figure 2 E-H). For all the samples, under  $\lambda_{\text{ex}} = 365$  nm the addition of iron oxide also quenches the luminescence response, with an additional red emission peak at 720 nm. **Chondrites**-All meteorites and the Type IV kerogen exhibit a strong blue photoluminescence emission between 450 – 490 nm and an additional red emission luminescence peak centred at  $\sim 720$  nm (Figure 3A), with a stronger response for CMs that have endured less thermal metamorphism. This is possibly the result of a higher maturity concentrating the chromophores (C=C and C=O bonds) and thus absorbs most of the luminescence [9].

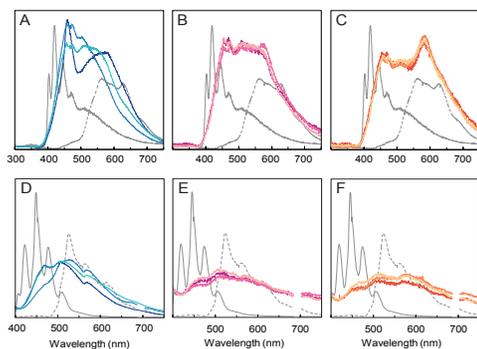


Figure 1: UV luminescence spectra of the pure Iceland sediment matrices (darkest colour) and those spiked with anthracene (mid-colour) and perylene (lightest colour) at  $\lambda_{\text{ex}} = 280$  nm (A-C) and  $\lambda_{\text{ex}} = 365$  nm (D-F) for Gypsum (Blue, A+D), Mudstone (Pink, B+E) and Oxide (Orange, C+F). Pure PAH luminescence spectra shown in grey (solid line = anthracene, dashed line = perylene).

For Murchison (face 2) and kerogen samples, the emission spectra become more resolved as excitation wavelength increases (figure 3B), as the number of resolvable peaks increases from 2 – 3 at the two shortest excitation wavelengths, to 5 resolvable peaks at the two longest excitation wavelengths.

#### 4. Acknowledgements

The authors thank the NHM London (Caroline Smith, Natasha Almeda) for the Murchison loan (MIN2017-674MET) and the NASA JSC ARES division (Kevin Righter) for the Antarctic meteorites (ID: person-924), as well as Zita Martins for her help for the meteorites acquisition. This work is funded by The Leverhulme Trust (RPG-2015-071).

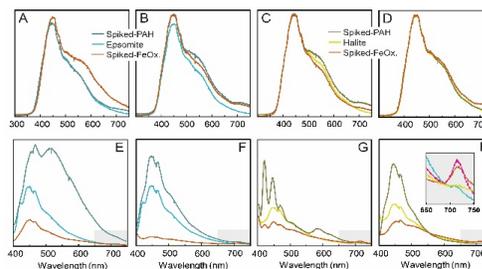


Figure 2: UV luminescence spectra of synthetic epsomite and halite at  $\lambda_{\text{ex}} = 280$  nm (A -D) and  $\lambda_{\text{ex}} = 365$  nm (E-H). Data are shown for crystals spiked with Anthracene (A, C, E, G) and Pyrene (B, D, F, H), and also with either PAH plus Fe oxyhydroxide (“Spiked-FeOx”).

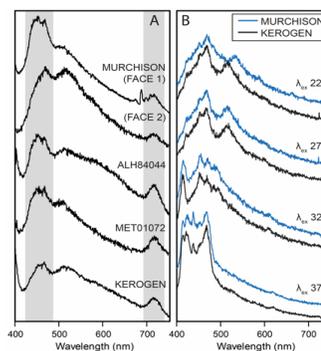


Figure 3: (A) UV luminescence spectra of carbonaceous chondrites and Type IV Kerogen, at  $\lambda_{\text{ex}} = 365$  nm and room temperature. Two faces of Murchison are shown, one with a large visible chondrule (“Face 1”) and one face without any visible chondrules (“Face 2”); (B) UV luminescence spectra of Murchison (Face 2) and type IV Kerogen for  $\lambda_{\text{ex}} = 225, 275, 325, 375$  nm.

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## Evolution of Organic Molecules in Pre-Solar Ice

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### Abstract

Comets and asteroids are the carriers of complex organics, some of which are the building blocks of life. However, we do not have a clear understanding where and how these complex organics produced, preserved, and transported – finally forming the interior of comets and asteroids. We have explored laboratory studies on analogs of interstellar and cometary ice and followed the reaction pathways of radiation-induced chemistry.

### 1. Introduction

Interstellar ice grains and cometary outgassing have so much in common that it is hard to understand how such compositional similarity is preserved without the interstellar ice grains themselves preserved throughout the evolution of our solar system – from dense molecular clouds through protoplanetary disk to evolved solar system that has the cometary precursors – Kuiper Belt Objects and Oort Cloud.

While the link seems to be obvious, chemical evolution of ice grains in the protoplanetary phase is far from well understood. Particularly, if the ice particles were to cross the ice-line towards the protostar and sublimate leaving the refractory grains behind. It is hard to determine how similar composition is put together in the formation of cometary precursors. We have been following reaction pathways that could be used as tracers for the history of ice grain chemistry and transport.

### 2. Results

We have carried out UV- and electron irradiation studies on water-rich ices containing other impurities such as

CO<sub>2</sub>. We have used polycyclic aromatic hydrocarbons (PAHs) as probes to understand how chemical modifications have been triggered through UV or electron irradiation. We have used conventional UV and FTIR spectroscopic methods as well as in-house-developed two-step two-color laser ablation and laser ionization time-of-flight mass spectrometry (2S-LAI-TOFMS).

We found that (a) PAH molecules are ionized efficiently, (b) even at 10 K these ionized PAHs react with reactive intermediates of water ice matrix (such as OH or O) forming oxygenated PAHs, (c) a wide range of complex organics are formed from simple ice mixtures such as water/methanol/ammonia, (d) most (if not all) molecules we detected in the laboratory study are found in Rosetta outgassing.

We have also studied the effect of significant amount of CO<sub>2</sub> co-condensed with H<sub>2</sub>O and found that PAHs are ionized even in CO<sub>2</sub> ice. These findings will be discussed in the context of how complex organics could have evolved, preserved, and transported across our solar system formation process.

### Acknowledgements

This work was carried out at the Jet Propulsion Laboratory, California Institute of Technology, was under a contract with the National Aeronautics and Space Administration (NASA). Funds were provided through NASA Solar System Workings as well as NASA funding through Rosetta (US).

# Solid state matter and chemical evolution in space. Insights from quantum chemical calculations

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## Abstract

Our universe is molecularly rich [1-3], comprising from the most essential molecules (such as  $H_2$ ,  $H_2O$  and  $NH_3$ ), passing through complex organic molecules (namely, COMs, molecules between 6 – 13 atoms where at least one is C rendering its organic character [4]), reaching more evolved complex organic compounds, in which in some cases are of biological relevance, such as amino acids, nucleobases and sugars. Formation of early Solar-type systems involves successive steps, mainly represented by the prestellar, protostellar, protoplanetary disk, and planetesimal and planet formation phases [5]. This evolution goes hand-in-hand with an increase of the molecular complexity, in which more complex molecules form at each step. A key role of this chemical evolution is played by cosmic solid state materials (CSSMs), as their surfaces provide catalytic sites that favor pivotal chemical reactions. For instance, in the prestellar phase, grains actively participate in several surface-induced reactions such as formation of  $CH_3OH$  by H-addition to CO [6], while in the protostellar phase, COMs can be formed on the surfaces of the ices during the collapse stage [7]. The current knowledge of the role of the CSSMs in the chemical evolution occurring in space is mostly based on spectroscopic observations, helped by laboratory experiments and astrochemical models. This combination has been fruitful to elucidate the chemical composition, broad structural features and chemical activity of CSSMs. However, they cannot provide atomic-scale information such as their detailed structure or the actual role in chemical reactions, a serious limitation to fully understand the fundamental steps leading to the chemical complexity in space. This limitation can be alleviated by adding a fourth level of investigation grounded on rigorous quantum mechanical methods. In this talk, a couple of examples demonstrating the relevance of these theoretical methods to obtain

quantitative atomic-scale information are presented. The first example concerns the formation of formamide ( $NH_2CHO$ ) as a COM test case. COMs formed on the surfaces of grains are believed to occur via radical-radical coupling [8], in the particular case of formamide by the coupling of  $NH_2$  with  $HCO$ . However, formation of  $NH_3+CO$  has been identified as a competitive path against formamide formation. Additionally, other mechanisms leading to formamide formation have also been identified, such as reaction between  $CN$  with  $H_2O$  molecules belonging to the ice mantles [9]. The second example is related to the interaction of a set of molecules belonging to different families of organic compounds identified in meteorites of the class of carbonaceous chondrites (CCs) with silicates. Quantum chemical calculations have allowed establishing an affinity scale of these compounds with the forsterite ( $Mg_2SiO_4$ ) silicate, one of the most abundant material present in both the matrix and chondrules of CCs. The affinities, based on the calculated binding energies of the organic compounds with the silicate, are compared with their abundances found in different meteorites [10].

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# UV induced methane and volatile organic carbon emission from the Murchison meteorite

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## Abstract

Meteorites and interplanetary dust can deliver organics to the Mars. The fate of these organics is poorly understood. Long-term (>100 hours) irradiation studies of the Murchison meteorite show the emission of previously-reported methane (CH<sub>4</sub>), along with 17 newly detected volatile organic carbons (VOCs), of which acetaldehyde, formaldehyde, and acetone/propanal are the most abundant. The data sheds new light on the contribution of extra-planetary material on the organic and CH<sub>4</sub> budgets of planets, e.g. Mars.

## 1. Introduction

The origin of CH<sub>4</sub> in the Martian atmosphere [e.g. 1] remains unclear. While on Earth the vast majority of CH<sub>4</sub> is biogenic, it is doubtful that this is the case on Mars. Other sources include release from clathrates [2] and emission as a photodegradation product of extra-Martian organic matter from meteorites and interplanetary dust particles [3], [4]. The possible contributions of these sources are poorly understood. To further investigate contributions of meteoritic CH<sub>4</sub>, long-term experiments were conducted to determine its emission rates along with other VOCs from the Murchison meteorite as a result of UV irradiation.

### 1.1 Materials and methods

Small (~100mg) samples of Murchison meteorite (carbonaceous chondrite, CM2) material were ground and placed in an airtight glass container. All glassware was rinsed with water (18.2MΩ), acetone, and methanol, wrapped in aluminium foil and heated to 550°C for 3 hours. The sample was irradiated with a Xe-arc discharge lamp through a UV transparent Suprasil window. The lamps intensity is about seven times stronger than UV intensity on the Martian surface in the 250-320 nm range and roughly five times stronger in the 320-400 nm range [5]. The

sample chamber was flushed with pure N<sub>2</sub> gas and not shaken during experiments. The outflowing gas mixture was split and led to a Picarro cavity ring-down spectroscopy (CRDS) CH<sub>4</sub> analyzer and a proton transfer reaction time of flight mass spectrometer (PTR-TOF-MS). The instruments measure CH<sub>4</sub> and VOCs every 5 and 1 seconds respectively. The data was analyzed using MatLab (CH<sub>4</sub>) and PTRwid [6] (VOCs). Emission rates were calculated from concentrations using Eq. 1.

## 2. Results and discussion

Experiments indicated that CH<sub>4</sub> is emitted from meteorite material instantaneously when UV irradiation starts. After 200 hours, emission is still ~20 times larger than background emission (Fig. 1). The emission rate is described with a 3-term exponential function ( $R^2=0.9985$  in Fig. 1). All six long-term experiments can be described by such a function,  $R^2$  values are >0.99 in every experiment. The terms of this exponential function contribute a few %, ~15%, and ~80% to the total methane emission. The fundamental causes for this specific fit are still under investigation. In addition to methane, other VOCs were also emitted (Fig. 2). We detected 17 distinct masses after background corrections. The most abundant VOCs are acetaldehyde, acetone and/or propanal (both are at mass 59), methanol and formaldehyde. Fitting the emission data of the VOCs is more challenging than CH<sub>4</sub> since the concentrations are much closer to the PTR-TOF-MS detection limit and noise is therefore high. Nevertheless, formaldehyde, methanol, acetaldehyde, and acetone/propanal are well described by the aforementioned 3-term exponent ( $R^2$  values of respectively 0.9927, 0.9346, 0.9892, and 0.9734). The mass of PTR-TOF-MS detectable VOCs was summed up and the total mass was three times higher than the total mass of CH<sub>4</sub>. However, the molar CH<sub>4</sub> to VOC ratio is roughly 1:1. The total mass of all emitted compounds over 103 hours is still <0.5 wt.% of the initially present organics in the Murchison meteorite,

assuming 2 wt.% total organics. VOC emission are likely to include ethane, propene, and propane, as reported by [3], but those compounds are not detectable using this setup. Furthermore, the abundance of formaldehyde has a large error that could well be larger than the reported concentration itself, as the measured concentration is strongly influenced by e.g. humidity. The detected photodegradation products sheds new light on the atmosphere as a sink for extra-Martian organics.

### 3. Figures

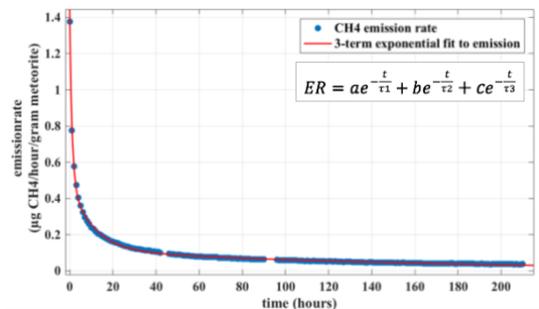


Figure 1: Plot of CH<sub>4</sub> emission rate against time.

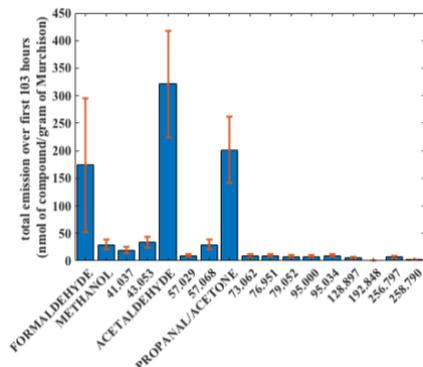


Figure 2: Total emitted VOCs after 103 hours of irradiation. Unidentified masses are protonated masses (+1 amu).

### 4. Equations

To calculate the emission rate ( $ER$ ) we use air flow in ml/min ( $f$ ), the concentration over background in ppm ( $\Delta C$ ), the molar volume of air in liters ( $V_{air}$ ), the molar mass of CH<sub>4</sub> in g/mol ( $M_{CH_4}$ ) and the sample mass in grams ( $m$ ) in Eq. 1.

$$ER = \frac{f * \Delta C * M_{CH_4}}{V_{air} * m} \quad (1)$$

### 5. Summary and Conclusions

Long-term experiments confirm the previously reported emissions of CH<sub>4</sub> from carbonaceous chondrites under UV irradiation. In contrast to the first extrapolations by [3], we show CH<sub>4</sub> emission is still measurable after more than 200 hours. The emission of CH<sub>4</sub> can be mathematically described by a 3-term exponential function. Besides CH<sub>4</sub>, VOCs are also emitted in a similar pattern. The mass of emitted VOCs is three times larger than the mass of emitted methane, while molar emissions are very similar to that of CH<sub>4</sub>. Acetaldehyde, acetone/propanal, formaldehyde, and methanol are the most abundant emitted VOCs.

### Acknowledgements

This study was funded by NWO grant ALW-GO/15-47.

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## From Diffuse Interstellar Bands to comets: the organic connection

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### Abstract

The analysis of dust grains collected by *Rosetta* spacecraft from comet 67/P Churyumov-Gerasimenko has shown that they are constituted of about the same amount of minerals and large organic molecules (in mass ~45% organic, ~ 55% mineral, ([2], Bardyn et al. 2017). We suggest that the comet organic molecules are the same organic molecules that produce, in the Interstellar Medium (ISM), diffuse absorption features imprinted on stellar spectra (DIBs, Diffuse Interstellar Bands). The large molecules forming the DIBs are not yet identified, except for fullerene  $C_{60}^+$ , but are thought to constitute "... the largest reservoir of organic material in the Universe" ([7], Snow, 2014).

### 1. Introduction

The COSIMA instrument on board *Rosetta* collected dust grains escaping from the nucleus of 67P. Their composition was analyzed with a SIMS-TOF technique. They all show  $C^+$ ,  $CH^+$ ,  $CH_2^+$ ,  $CH_3^+$ , which are fragments of much larger unidentified organic molecules ([6], Fray et al., 2015). We propose that they are the same large molecules producing the DIB absorptions in the ISM that agglomerate together in a condensing interstellar cloud which became eventually our solar system ([3], Bertaux et Lallement, 2017). Therefore, there is no need to invoke a massive fabrication of organics during the solar system. They were conserved from ISM during the formation of the solid comet nucleus, within the scenario established by [4] Davidsson et al. (2016) based on many arguments collected by *Rosetta*: a hierarchical scenario of gentle accretion of small interstellar grains to the final size of the nucleus. We back up our suggestion from both qualitative and quantitative arguments.

### 2. The ratio organic/mineral

A statistical analysis of the Equivalent Width (EW) of all known DIBs absorptions was performed. Assigning to all DIBs an oscillator strength equal to  $C_{60}^+$  and an average number of 60 C atoms per DIB carrier molecule, it is computed that at least 30% of ISM carbon is locked into a DIB carrier. It implies that in the ISM, the ratio organic/mineral is at least  $R_{ISM}=0.32$ , to be compared to  $R_C=0.8\pm 0.1$  for the comet [2]. For the ISM,  $R_{ISM}=0.32$  is a lower limit, since only those organic molecules which absorb are accounted for.

### 3. DIB carriers decrease within dense clouds

On the other hand, the sounding of some interstellar nebulae show that, when the Line-of-sight approaches the centre, the DIBs depths are levelling off while the dust extinction is still increasing, suggesting an accretion process for the DIB molecules. These organic molecules would agglomerate to form interstellar grains that will end up in the proto-solar nebula, then in comet nuclei.

As an example of such an accretion process in the ISM, the EW of an infra-red DIB has been compared to the dust extinction in the Barnard 68 nebula [5]. On fig.1 is represented the distribution of dust extinction (taken from [1]) which increases toward the center of the nebula. The dust extinction and corresponding H columns may be plotted as a function of distance to center (not shown here). They then may be inverted by an onion-peeling method to yield the local density distribution function of [H] as a function of distance to center (in arcsec, figure 2). The same method was applied to the EW of the IR band at 1527.3 nm, to derive a local volume density of this particular DIB carrier associated to this IR DIB.

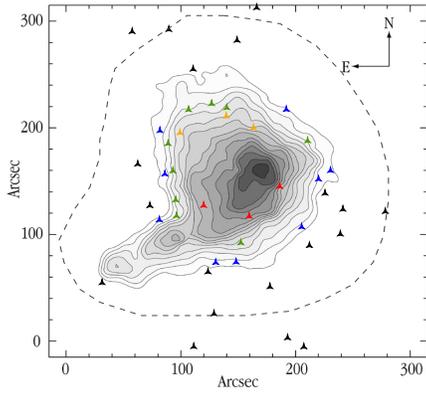


Figure 1: Target positions on the Barnard 68 extinction map from [1]. Solid contours correspond to 2 magnitude steps from extinction  $A_V = 4$  to 30 mag. The dashed line represents  $A_V = 1:2$  mag (taken from [5]).

While the local densities of both H atoms and DIB carriers are increasing toward the center of the nebula (figure 2), the increase of DIB carriers is much slower than the H atoms, as displayed by their ratio  $n(H)/n(DIB)$  which *decreases* toward center (blue curve of figure 2). This fact may be interpreted by an accretion process of DIB carriers molecules, either aggregating between themselves or accreting onto dust grains. Once these molecules are accreted, they can no longer absorb as they were when free-floating in space before accretion. Once formed, these grains (which could contain also minerals) would constitute the major fraction of the proto solar system from which condensed comet nuclei.

## Conclusions.

It is often stated that early bombardment of comet nuclei on Earth could have facilitated the emergence of life on this planet by bringing organic material. Comet 67/P contains 3.5 billion tons of organic matter. Since the presence of DIBs is ubiquitous in our Galaxy, and in other galaxies, it is likely that organic material has been brought to all habitable exo-planets. How many of them have developed life, and intelligent life, are two other questions that would deserve large research investments, since they are related to the layman question: “Are we alone in the Universe?”

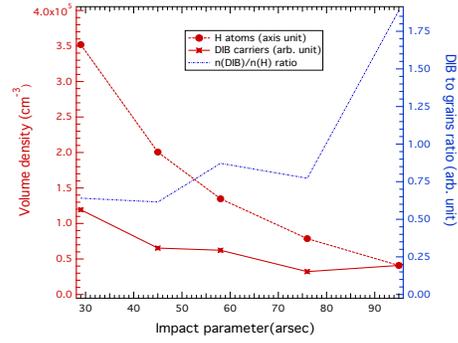


Figure 2: Volume density of DIB carrier  $n(DIB)$  based on the simplified inversion of EWs (left scale). Also shown is the inverted volume density  $n(H)$  based on  $A_V$  data. The  $n(DIB)$  has been artificially scaled in such a way the two curves cross for the external layer at 96 arcsec. The ratio between the DIB carrier and H volume densities is also shown (right scale): it decreases toward center (taken from [5]).

Our proposed scenario of DIB connection with comets implies that a comet return-sample mission would not need to be much cooled to keep the double interest for comets and for Interstellar Medium studies, since the solid organic phase of the comet is not very volatile.

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# Study of organic compounds present in the NorthWest Africa 6148 Nakhlite by means of Raman spectroscopy

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## Abstract

Even though the rovers of the upcoming missions to Mars already have specific instruments for the analysis of organic compounds, Raman spectroscopy is also a suitable technique to provide supplementary information to these other instruments. In this work, several bubbles containing organic compounds have been detected using this technique on the NWA 6148 Martian meteorite. The bubbles contain a complex mixture of carboxylic acids, along with other organic compounds. Raman spectroscopy was used in the high resolution image mode to draw the shape of the bubbles in the context of an olivine matrix.

## 1. Introduction

Since one of the main objectives of the upcoming Mars missions (ExoMars 2020 from ESA and Mars 2020 from NASA) is to elucidate the possible existence of past life in the planet, instruments and techniques capable of detecting and identifying both organic compounds and biomarkers are essential. The main instrument designed with this purpose in the ExoMars 2020 rover is the MOMA. However, other instruments that are present in the rover could be used, as well, with this aim as a secondary or support technique. They would be used to contrast and confirm the information obtained from MOMA regarding organic compounds. In this work we illustrate how Raman spectroscopy can be useful to detect and characterize prebiotic, abiotic or biotic organic compounds.

In order to test the capabilities of the technique in this regard, the NorthWest Africa (NWA) 6148 nakhlite was studied. As a Martian meteorite, the mineral distribution and morphology is like that on the Red Planet, thus, its study provides information of what kind of results Raman spectroscopy can provide when studying organic compounds in Martian rocks.

## 2. Sample description

The analysed NWA 6148 sample weights 0.246 g and has dimensions of about 5x7x3 mm. It has not visible impact crust and is brownish with several greenish, black and light brown areas. As other nakhrites, it is mainly composed of augite formed from basaltic magma. It also contains olivine rich in iron as the second most abundant mineral. A complete geochemical study of this sample can be found in literature [2].

## 3. Methodology

To carry out the study of the organic compounds present in the NWA 6148, an InVia confocal micro-Raman spectrometer (Renishaw, UK) was used. A 532 nm excitation laser was employed to acquire the spectra, both in a point by point and high resolution image mode. The WiRE 4.2 software (Renishaw, UK) was used to process and obtain the information of interest from the Raman images.

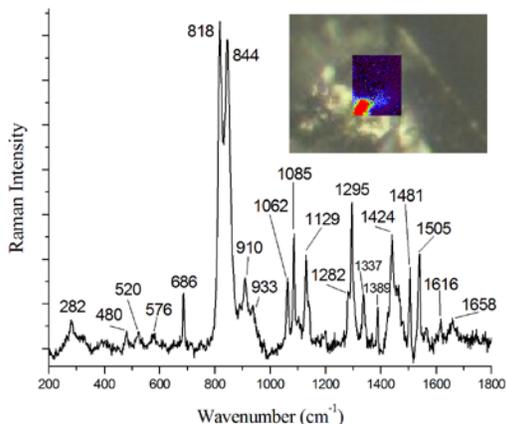
In order to find the bubbles and cavities where the organic compounds were present, a SEM-EDS instrument was used with an SCA interface, which allows performing Raman analysis in the desired spots of the SEM-EDS images.

## 4. Results and Discussion

After an in-depth analysis of the NWA 6148 sample, several bubbles containing organic compounds were detected. Figure 1 shows one of the mentioned bubbles with the Raman image mapping the organic signature bands. The Raman image is composed of 4280 individual spectra, from which almost 500 are the ones with bands of organic compounds (in red in Figure 1, each pixel of the Raman Image corresponds to an individual spectrum).

As can be observed, Raman spectra can be difficult to interpret in terms of organic molecules, especially

if there is more than one compound present simultaneously in the same spot. However, in the case of this bubble, the  $\nu(\text{C-C})$  stretching vibrations of carboxylic acids of 8 or 10 atoms of carbon are observed in the 1062, 1085 and 1129  $\text{cm}^{-1}$  bands. Moreover, the 1295  $\text{cm}^{-1}$  band is typical of  $\delta(\text{CH}_2)$  twist vibrations of these acids and the bands at 1389, 1461 and 1505  $\text{cm}^{-1}$  are assigned to  $\delta(\text{CH}_2)$  or  $\delta(\text{CH}_3)$  deformations, all of them typical from linear saturated carboxylic acids [1].



**Figure 1.** Average Raman spectrum of a mixture of organic compounds contained in a bubble (red), over the Raman signature of an olivine matrix.

Nonetheless, if several spectra are analysed separately and not as an average spectrum of the whole bubble, more differences can be appreciated. Table 1 shows the normalized area, using the 1295  $\text{cm}^{-1}$  band area as a normalizing factor, of several Raman bands corresponding to three Raman spectra from a bubble from the NWA 6148. As it can be observed, several areas of the different bands are not proportional from one to another. For instance, the 1062 and 1129  $\text{cm}^{-1}$  bands ( $\nu(\text{C-C})$  stretching vibrations, correlated with the number of carbon atoms in the organic acid chain), is much larger in spectrum 1 than in 2 or 3. However, in the case of the bands assigned to  $\delta(\text{CH}_2)$  or  $\delta(\text{CH}_3)$  deformations of linear carboxylic acids, the 1389  $\text{cm}^{-1}$  band is larger in spectrum 1, although in the case of the 1505  $\text{cm}^{-1}$  it is the smallest one. Other bands, such as the ones at 520 or 686  $\text{cm}^{-1}$  are similar from one spectrum to another. All these facts mean that even though the initial guess could not be wrong (carboxylic acid of short chains is present in the bubble), the bubble could be filled by a complex mixture of compounds of similar nature.

**Table 1.** Normalised area of some organic signature bands of three different Raman spectra obtained from an analysed bubble.

Raman band ( $\text{cm}^{-1}$ )	Normalized Band Area		
	Spectrum 1	Spectrum 2	Spectrum 3
520	0.70	0.43	0.20
686	0.27	0.30	0.54
1062	5.00	0.49	0.98
1085	0.40	0.49	0.46
1129	3.83	0.59	1.20
1295	1.00	1.00	1.00
1337	2.83	0.56	1.16
1389	7.60	0.18	0.61
1461	2.65	0.96	3.63
1505	0.13	0.41	0.38

## 5. Conclusions

Raman spectroscopy has been proven as a useful technique in order to study bubbles or cavities where organic compounds are present in Martian meteorites. In the current example, it was possible to characterize the nature of the organic compound present in the sample. In addition, it was observed that the bubble has a complex mixture of organic compounds, mainly saturated carboxylic acids. As a disadvantage, Raman spectroscopy has nowadays difficulties to characterize organic compounds of the same nature, as well as to quantify said compounds. For that purpose, new developments are required.

## Acknowledgements

This work has been financially supported through the Exomars-Raman project (ref. ESP2017-87690-C3-1-R), funded by the Spanish Agency for Research AEI (MINEICO-FEDER/UE).

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# Photocatalytic Properties of Minerals and their Role in Prebiotic Chemistry

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## Introduction

A myriad of astrophysical environments, once thought to be barren of anything but hydrogen and helium, are now known to be rich in complex carbon chemistry. Not only are carbon molecules such as amino acids and polycyclic aromatic hydrocarbons (PAHs) present in interstellar space, but also on the rocky bodies of our Solar System, as confirmed by the species found in the Murchison and other meteorites. When these organic molecules are adsorbed to their mineral substrates, they undergo a different chemical evolution than they would in gas phase. The resulting reactions play a part in generating organic species important to the inventory of prebiotic chemistry on the early Earth, Mars, asteroids, and comets. In this PhD project, we specifically focus on photocatalysis: how iron and magnesium bearing minerals act as catalysts to accelerate the destruction of PAHs by radiation.

## Experimental

The project aims to experimentally constrain photocatalysis products of selected extraterrestrially formed PAHs under a realistic range of UV-Vis radiation doses representative for early Earth, Mars, asteroids and cometary surfaces, and subsequently assess the reaction products of PAH-mineral aggregates. Our findings will be critical for interpretation of data from the Mars Organic Molecule Analyzer instrument (MOMA) onboard ESA's 2020 ExoMars rover and the Raman instruments onboard ExoMars and NASA's Mars2020 rover. They will further enable the development of a next generation of detectors of planetary organics.

To achieve this, irradiation experiments are performed in PALLAS (the Planetary Analogs Laboratory for Light, Atmosphere, and Surface Simulations) [ten Kate & Reuver, 2015]. In these experiments two types of PAH-mineral aggregates are exposed to UV light, without and with water as a binding agent. The analytical techniques used include Fourier transform infrared (FTIR) spectroscopy, Raman spectroscopy, as well as gas chromatography mass spectrometry (GCMS). An example of the FTIR and Raman spectra is shown in Figure 1.

## Background

In the presence of UV and Vis radiation certain mineral surfaces can display a photocatalytic effect, a well-known process in the semi-conductor field [Fox and Dulay, 1993]. This effect is characterised by the mineral surface acting as a catalyst that accelerates the photoreaction, generally resulting in the destruction of the attached organic molecules. The photocatalytic activity of a catalyst depends on its ability to create electron-hole pairs where reaction of the holes with adsorbed water molecules create OH free radicals that oxidize organic compounds [Fujishima et al., 2000]. Electron-hole pairs can also induce oxidizing reactions without creating free radicals by involving chemisorbed molecules that serve as hole traps [Shkrob et al., 2011a]. Here, we investigate the relevance of these effects in conditions of the early Earth, Mars, asteroids, and comets.

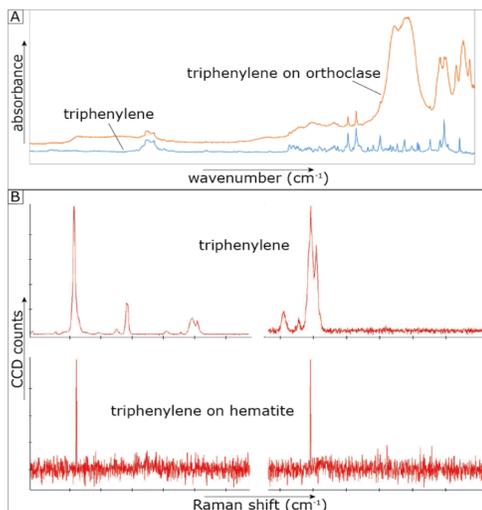


Figure 1. Preliminary (A) DRIFTS and (B) Raman spectra of both pure triphenylene and triphenylene adsorbed onto orthoclase (A) and hematite (B).

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# Interstellar Fullerenes

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## Abstract

In this contribution we present recent results on the detection and study of fullerenes (and related molecular species) in the diffuse-to-translucent interstellar medium. The results pertain primarily to new observations of interstellar targets obtained with both ground- and space-based facilities operating in the optical and infrared wavelength domains.

## 1 Interstellar fullerenes

Following the recent laboratory confirmation of two interstellar absorption bands arising from the  $C_{60}$  cation it is now possible to systematically study the presence and abundances of interstellar fullerenes in context of the general, largely unidentified, organic inventory of the interstellar medium (ISM).

The near-infrared spectral signature of  $C_{60}^+$  is studied at high-spectral resolution ([4]) with UVES & CRILES instruments at the VLT and ESPADONS at the CFHT. Furthermore, near-infrared observations from space with the STIS instrument on the Hubble Space Telescope ([2]) allow an unobscured view of this range that is normally, for ground-based observations, heavily contaminated by telluric features. We present results on our astronomical search for the weaker  $C_{60}^+$  bands predicted by laboratory experiments. In addition we discuss the properties (profile substructure) of the two strongest bands. Furthermore, a careful analysis of archival Spitzer space telescope mid-infrared IRS spectra revealed the presence of neutral  $C_{60}$  bands in two regions probing the diffuse and the translucent ISM ([1]). The derived abundances for  $C_{60}$  emission and absorption are in agreement. Finally, we discuss the implication of these recent detections of fullerenes in space for our understanding of the organic inventory of the ISM, in particular in the context of the long-standing enigma concerning the identity of the carriers of the diffuse interstellar bands (DIBs) ([3]).

## 2. Summary and Outlook

The recent laboratory confirmation of  $C_{60}^+$  as the carrier of two prominent near-infrared DIBs has re-newed interest in the enigma of the identity of the DIB carriers and offers a fresh view on the chemical complexity of interstellar matter and its organic components. Future facilities like the James Webb Space Telescope will allow us to obtain very sensitive infrared emission spectra of low-density diffuse interstellar gas & dust clouds. Furthermore, advances in near-infrared high-resolution spectroscopy and atmospheric modelling of telluric lines will allow us to probe more deeply the physics of  $C_{60}$  in space and map their presence in the Milky Way, Local Group galaxies and beyond.

## Acknowledgements

This research is based on observations collected with the Very Large Telescope, and the Spitzer and Hubble Space Telescopes. We thank in particular Olivier Berné, Christine Joblin, Giacomo Mulas, and Rosine Lallement for the fruitful collaborations.

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## Organic molecules in protoplanetary disks

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### Abstract

Planets and comets formation occurs through the combination of dust and gas lying within the disks surrounding young stars. Among the molecules found in comets, some of them have also been detected in the interstellar medium (ISM). This leads one to ask whether these molecules were altered or formed in the protosolar nebulae or whether they are of direct ISM heritage. Consequently, understanding the formation of organic molecules, especially those of prebiotic interest, and the mechanisms that lead to their incorporation in asteroids and comets, might very well be of crucial importance for understanding the emergence of life. Thanks to recent progress in radioastronomy instrumentation for (sub-)millimeter arrays (i.e. high angular resolution and high sensitivity), such as with ALMA, new results have been obtained. I will review some notable results on the detection of organic molecules, including prebiotic molecules, towards protoplanetary disks.

### 1. Introduction

One of the major problem in Astrochemistry is whether the organic chemistry during the star and planet formation process is inherited by planets and small bodies of the final planetary system. And in an interstellar-Earth connection, what the key organic molecules are?

At the present time, only about twenty molecules have been detected in protoplanetary disks as shown in Table 1. Among the complex one, there are hydrocarbons, such as  $c\text{-C}_3\text{H}_2$  (Qi et al. 2013b; Bergin et al. 2016), cyanides,  $\text{HC}_3\text{N}$  and  $\text{CH}_3\text{CN}$  (Chapillon et al. 2012; Öberg et al. 2015), and the following organic O-bearing molecules, methanol,  $\text{CH}_3\text{OH}$  (Walsh

et al. 2016), and formaldehyde,  $\text{H}_2\text{CO}$  (Qi et al. 2013a; Öberg et al. 2017). The latter are important for complex organic chemistry. These finding show that the search for large organic molecules (COMS) in protoplanetary disks still remain challenging.

### 2. ALMA observations of COMS in TW Hya

We performed a deep search for formic acid ( $\text{HCOOH}$ ), a key organic molecule for Life on Earth along with the  $c\text{-C}_3\text{H}_2$ , using the unprecedented sensitivity of the Atacama Large Millimetre/Submillimetre Array (ALMA). I will present our detections towards the protoplanetary disk surrounding the closest Solar-type young star TW Hya (Favre et al. submitted to ApJL).

### 3. Summary and Conclusions

Along with the detection of methanol and cyanide in the same protoplanetary disk, our study shows that complex organic chemistry is taking place in objects where planet formation occurs.

### Acknowledgements

This work was supported by (i) the Italian Ministry of Education, Universities and Research, through the grant project SIR (RBSI14ZRHR), (ii) funding from the European Research Council (ERC), project DOC (The Dawn of Organic Chemistry), contract 741002 and (iii) the project PRIN-INAF 2016 The Cradle of Life - GENESIS-SKA (General Conditions in Early Planetary Systems for the rise of life with SKA).

## Molecular inventory of protoplanetary disks

<b>Atoms</b>	
C <sup>+</sup> , O	Meeus et al. (2012)
<b>Ions</b>	
HCO <sup>+</sup> , H <sup>13</sup> CO <sup>+</sup> , DCO <sup>+</sup> , N <sub>2</sub> H <sup>+</sup> , CH <sup>+</sup>	Dutrey et al. (1997, 2007), van-Dishoeck et al. (2003), Thi et al. (2011), Qi et al. (2008, 2013), Öberg et al. (2015a)
<b>Carbon reservoirs?</b>	
CO, CO <sub>2</sub>	Koerner & Sargent (1995), Pontoppidan et al. (2010)
<b>Simple species</b>	
<sup>13</sup> CO, C <sup>18</sup> O, OH, HD	Dutrey et al. (1996), Pontoppidan et al. (2010), Bergin et al. (2013), Favre et al. (2013), McClure et al. (2016)
<b>S-bearing molecules</b>	
CS, SO	Dutrey et al. (1997), Guilloteau et al. (2013)
<b>N-bearing molecules</b>	
CN, HCN, HNC, DCN	Dutrey et al. (1997), Qi et al. (2008)
<b>Carbon chains</b>	
CCH, C <sub>2</sub> H <sub>2</sub> , c-C <sub>3</sub> H <sub>2</sub> , HC <sub>3</sub> N	Dutrey et al. (1997), Pontoppidan et al. (2010), Henning et al. (2010), Chapillon et al. (2012), Qi et al. (2013) Öberg et al. (2015b)
<b>Water</b>	
H <sub>2</sub> O	Bergin et al. (2010), Hogerheijde et al. (2011), Podio et al. (2013)
<b>O-bearing molecules</b>	
H <sub>2</sub> CO	Öberg et al. (2017)
<b>Complex molecules</b>	
CH <sub>3</sub> OH, CH <sub>3</sub> CN	Walsh et al. (2016), Öberg et al. (2015)

Figure 1: Table 1 - Molecular inventory of protoplanetary disks.

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## Liquid hydrocarbons at the surface of Titan: bubbling or not bubbling?

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### Abstract

In the polar regions of Titan, the main satellite of Saturn, hydrocarbon seas have been discovered by the *Cassini-Huygens* mission. RADAR observations have revealed surprising and transient bright areas over Ligeia Mare surface. As suggested by recent research, bubbles could explain these strange features. However, the nucleation and growth of such bubbles, together with their RADAR reflectivity, have never been investigated. All of these aspects are critical to an actual observation. We have thus applied the classical nucleation theory to our context, and we developed a specific radiative transfer model that is appropriate for bubbles streams in cryogenic liquids. According to our results, the sea bed appears to be the most plausible place for the generation of bubbles, leading to a signal comparable to observations. This conclusion is supported by thermodynamic arguments and by RADAR properties of a bubbly column. The latter are also valid in the case of bubble plumes, due to gas leaking from the sea floor.

### 1. Introduction

After the arrival of *Cassini/Huygens* in the Saturn system, hundreds of lakes and seas of hydrocarbons were detected in Titan's polar regions (Stofan et al. 2007). One of the northern seas, Ligeia Mare, has shown a strange property: ephemeral RADAR bright areas, nicknamed "Magic Islands," which appear and disappear from one flyby to another (Hofgartner et al. 2014, Hofgartner et al. 2016). Several ideas have been proposed to explain these transient features. Up to now, only scenarios based on streams of bubbles, due to the nitrogen exsolution, seem to possess a firm physical basis (Cordier et al. 2017, Malaska et al. 2017). Indeed, Titan's seas are probably composed of methane and some ethane, in which atmospheric nitrogen can easily dissolve. The existence of such bubbly plumes is not

extravagant, since bubbles of methane megaplumes are observed in Earth's oceans (Leifer et al. 2015, Leifer et al. 2017). To be efficient RADAR waves reflectors, bubbles must be of a size roughly the same as the RADAR wavelength, *i.e.* 2.2 cm. Here, we focus our purpose on bubbles nucleation and growth, and on bubble plume reflectivity.

### 2. Lakes and Maria Composition – Possible Mechanisms of Bubbling

Since the Kuiper detection of methane and the flyby of *Voyager* probe, we know that the atmosphere of Titan is meanly composed by nitrogen and methane, with respective mole fractions around 95% and 5%. At ground level, the thermodynamic conditions, *i.e.* 90-94 K and a pressure of 1.5 bar, are close to the methane triple point, letting the latter being liquid. Beside, due to the solar UV irradiation and the bombardment by energetic particles trapped in Saturn magnetosphere, methane and nitrogen molecules are broken, forming highly reactive radicals. These entities react with nearby molecules, initiating a complex organic chemistry (Lavvas et al. 2008a,b). The main products of this active photochemistry is ethane, which is also liquid under the conditions of Titan surface. Thus, the bulk composition of Titan Maria and lakes should be a liquid mixture of methane, ethane, with some amount of dissolved nitrogen (Dubouloz et al., 1989, Cordier et al., 2009, Tan et al., 2013). Many other compounds may dissolve in this organic cryogenic solvent, and may also be retrieved as evaporite deposits over lake banks or in dry lake beds (Barnes et al., 2011, Cordier et al. 2013, 2016).

For decades, it is known that ternary can undergo phase splitting, forming three distinct phases: two liquids, of different compositions, and one vapor phase (Lu et al., 1970, Fig. 1). This process, for some

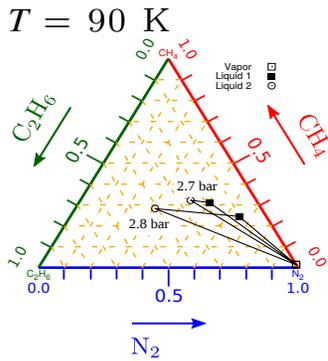


Figure 1: Diagram representing a ternary system  $N_2$ - $CH_4$ - $C_2H_6$ , with co-existence of three phases: two liquids and a vapor.

species, occurs in conditions close to room conditions, whereas others required significantly different conditions. In the case of Titan's Maria or lakes, the phase splitting of the cryogenic solution needs pressure slightly higher than the surface pressure, *i.e.* values around  $\sim 3$  bars. These conditions may be found in the depths of Titan seas, where, due to internal circulation of the fluid, time to time, an ephemeral formation of ternary equilibria may occur. The expelled nitrogen form bubbles with a maximum radius around 2 cm, consistent with a Cassini radar detection (Cordier et al., 2017).

### 3. Nucleation, Growth and RADAR Signature of Bubbles in Titan's Seas

Prior to get an equilibrium state, involving two or more phases, embryonic bubbles, or droplets, have to be created. The very first step of phase transition, called nucleation, has been studied in the present work. In the context of Titan's seas, two alternatives exist: an homogeneous nucleation and an heterogeneous nucleation. In the first case, bubbles appear in the volume of the liquid, while in the second case, the presence of some piece of solid material is required. We show that homogeneous nucleation is practically impossible, but, the seabed offers a favorable place for heterogeneous nucleation.

In a second step, bubbles have to grow in order to get sizes large enough to be radar detectable and explained the phenomenon of "Magic Island". We

have demonstrated the unefficiency of growing by diffusion of nitrogen. Indeed, this process requires a supersaturated liquid layer relatively deep, which poses the problem of its appearance. The presence of centimeter-sized bubbles, due to bubbles coalescence within the stream, has been also studied, and it offers a plausible opportunity of building up such large bubbles.

Finally, we developed a two stream model of radar wave scattering by a population of bubbles distributed in a column of liquid.

### 4. Summary

Titan presents an unique object where organic matter is massively present in liquid state at the surface. Several efforts have been made by the community to understand their composition, it appears that the mixtures of methane and ethane may be a good solvent for other heavier species. Beside, the observed liquid bodies have several strange properties, among them the "Magic Island" may be explained by a phase splitting in the depth of the seas. More widely speaking, the polar regions of Titan may harbor system that could be the prototypes for other system, existing at the surface of exoplanets, and open the door to a new kind of oceanography.

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# Development and realization of a spatialized micro LC for the analysis of biomarkers

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## Abstract

Search for organic matter in the solar system has become a key challenge in planetary exploration in order to understand whether they played a role in the origin and evolution of life on Earth. To date, instruments dedicated to the in situ analysis of organic compounds are essentially gas chromatographs [1]. These methods, applied to the study of extraterrestrial objects, such as comets or analogs, have demonstrated that these are formed of thousands of different chemical compounds [2–4]. However, GC does not allow the direct detection of biopolymers (peptides, nucleotides ...) yet essential as markers of the living.

Complementary study made with Liquid chromatography could provide a more comprehensive analysis of molecular structure by separating a large set of compounds. Studies have already been carried out in the laboratory on cometary analogues and they have confirmed the presence of compounds of high molecular masses [5] thus once again demonstrating the interest of these methods for astrobiological studies.

In this line, this work presents the development of a micro LC for the in situ analysis of high molecular weight compounds.

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