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# **Laboratory experimental simulations: Chemical evolution of the organic matter from interstellar and cometary ice analogs**

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**Abstract:** This contribution addresses the different approaches that are developed in our laboratory to study the chemical evolution of organic matter in stellar or interplanetary environments. In the first approach, starting from interstellar or cometary ice analogs subjected to different energy processes (thermal, photochemical), we aim to explain the mechanism of formation of key molecules (RING project: Reactivity in INterstellar ice Grains) such as HMT, POM or amino acid precursors that are or may be detected in future space missions. In a second approach, we are interested in the detection of volatile molecules sublimating from ice analogs when these latter are heated and/or irradiated (VAHIA project: Volatile Analysis from the Heating of Interstellar Ice Analogs) through an online experimental device coupling the simulation chamber where ices are formed to a GC-MS instrument. The objective is thus to simulate the effects of the ice material warming when a young star forms or when a comet becomes active. This project provides an inventory of molecules that can be found in hot corinos or in the gaseous phase of comets. In a third approach, we analyze the organic matter contained in the refractory residues that can be considered as cometary analogs (RAHIA Project: Residue Analysis from the Heating of Interstellar Ice Analogs) using very high resolution mass spectrometry (VHRMS). The results of these analyses show that residues present an important molecular diversity. This technique gives also the possibility to determine the elementary composition of these residues that can be compared to the meteorite composition. These residues can then be a basic material to develop, in a specific planetary environment, a prebiotic chemistry.

## **1 Introduction**

Dust grains found in cold and dense molecular clouds play an important role in the chemical evolution of the organic matter in star forming regions and comet environments. By accretion of the main elements (H, O, C, N,...) and molecules on silicate and carbonaceous material cores, followed by diffusion and surface reactions, thick icy mantles are built up. They consist of water (the dominant molecule), ammonia (the main nitrogen source), methanol (the most abundant organic molecule) and

other molecules such as  $\text{H}_2\text{CO}$ ,  $\text{HCOOH}$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{CH}_4$ ... (Gibb et al. 2000, Boogert et al. 2004, Dartois 2005, Zasowski et al. 2009). To date only about ten molecules have been detected in icy grains by IR satellites in the line of sight of young stellar objects (YSOs) due to the difficulty to detect species less than 1% with respect to  $\text{H}_2\text{O}$ . Primitive ices then evolve during the different phases accompanying the formation of low-mass stars and planetary systems like our solar system (Van Dishoeck & Blake 1998, Caselli & Ceccarelli 2012). When a dense cloud collapses due to its own gravity, a young star (protostar) surrounded by an envelope of gas and dust is formed in a process that can take about  $10^4$ - $10^5$  years. The formation of this protostar involves a warming effect of the ices, producing refractory compounds which form a residue after the sublimation of the most volatile compounds, in a region called hot corinos, located in the inner envelope around the protostar. Other effects such as cosmic rays bombardments, X rays or VUV radiations coming from the central star or the stars around can affect these grains and alter their chemical composition at different stages of their evolution. After about  $10^6$  years, the envelope leads to the formation of a disk in rotation, where dust grains will be distributed along the median plane of the star. By coagulation these dust grains will form larger bodies called planetesimals, then finally a planetary system with planets, satellites and comets, a process that will take several million years (Figure 1).

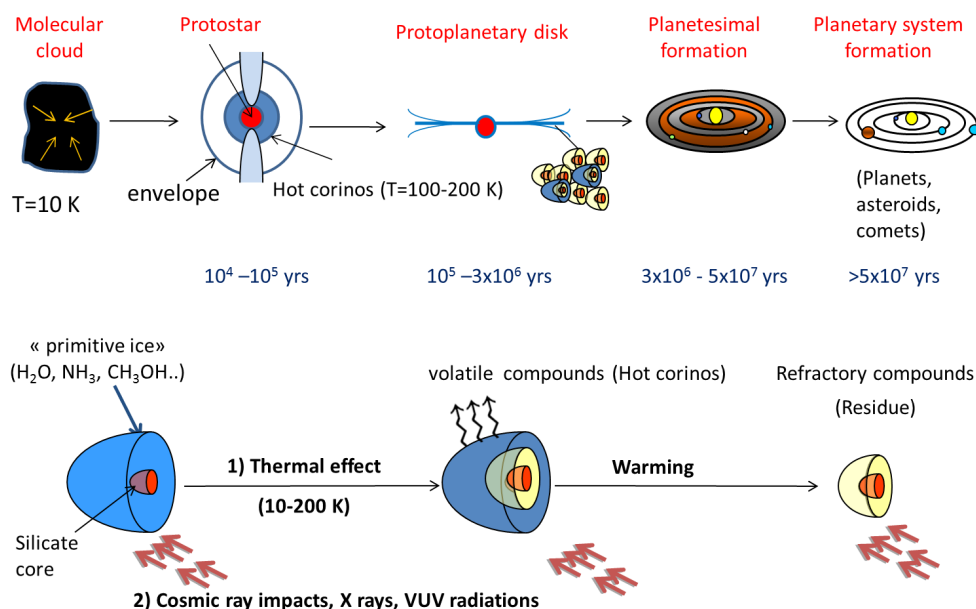


Figure 1: Organic material evolution from primitive ice to refractory compounds through the different phases of evolution of the objects (from dense molecular clouds to planetary systems).

In our group, we are interested in tracing the history of the chemical evolution of organic matter using simulation experiments in the laboratory and one of the main issues of this topic is the degree of molecular complexity that chemical species can reach in different astrophysical environments. To account for this evolution we have developed three approaches. In a first mechanistic approach, (RING project : Reactivity in INterstellar ice Grains), we aim to explain the relationship between detected or likely to be detected molecules in different astrophysical environments (hot corinos, protoplanetary disks, comets and meteorites) and constituents of primitive ices subjected to different effects (thermal or VUV irradiation processes). We are interested in the mechanism of molecule formation such as hexamethylenetetramine (HMT) and its derivatives, some polymers, amino acids and their precursors that can be considered as target molecules for space missions such as the Rosetta mission. During these studies, we perform isothermal kinetics or temperature programmed reactivity (TPR) experiments in order to measure reaction rate constants and activation energies. These experiments

are also complemented by quantum calculations in order to determine the nature of the intermediates and the reaction energetic profile. Temperature programmed desorption (TPD) experiments are also performed to measure the desorption energy of reactants and products formed. All these measurements are valuable to perform numerical simulations and to determine the conditions of observation of molecules in various objects. In a second approach, we determine through the VAHIIA (Volatile Analysis from the Heating of Interstellar Ice Analogs) project species sublimating from the grain during the heating of interstellar or cometary ice analogs. These experiments are useful to establish a full screening of molecules that can be detected in the gaseous environment of stars (hot cores/corinos) and comets, but also to assist in the data processing of space missions and to propose new molecules to observe in astrophysical environments. In a third approach, we determine through the RAHIIA (Residue Analysis from the Heating of Interstellar Ice Analogs) project the composition of the organic matter contained in the refractory residues that can be considered as cometary or meteoritic grain analogs. These residues can be regarded as a material source from which, in an environment like the primitive Earth, prebiotic chemistry may start.

## 2 The experimental device used for simulation experiments

The experimental device used to reproduce interstellar or cometary ice analogs is based on an experimental concept, matrix isolation spectroscopy. A gas mixture with the molecules detected around protostars (e.g.  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$ ,  $\text{NH}_3$ ,  $\text{CO}$ ,  $\text{CO}_2$ ...) is prepared in a vacuum glass ramp, and then deposited onto a copper-plated surface cooled to the desired temperature (10-80 K) inside a cryogenic chamber under a high vacuum pressure ( $10^{-9}$  mbar). In these conditions an ice analog is formed on the surface. A microwave discharge hydrogen flow lamp producing VUV radiation can be used to mimic the effects induced by the central star and other stars around. Considering the lamp flux ( $2 \cdot 10^{14}$  photons  $\text{cm}^{-2} \text{s}^{-1}$ ), 1h of irradiation has a similar effect to  $10^6$  years of irradiation in star forming regions. The evolution of the ice composition is followed by FTIR spectroscopy during the irradiation but also during the subsequent heating which leads to volatile compounds that can be characterized with a QMS mass analyzer for a simple mixture, or separated and then characterized using a GC-MS device for a complex mixture. At the end of the experiment, after a warming-up to 300 K, an organic residue is obtained which can be recovered and stored prior to its analysis. An overview of the experimental device is displayed in Figure 2.

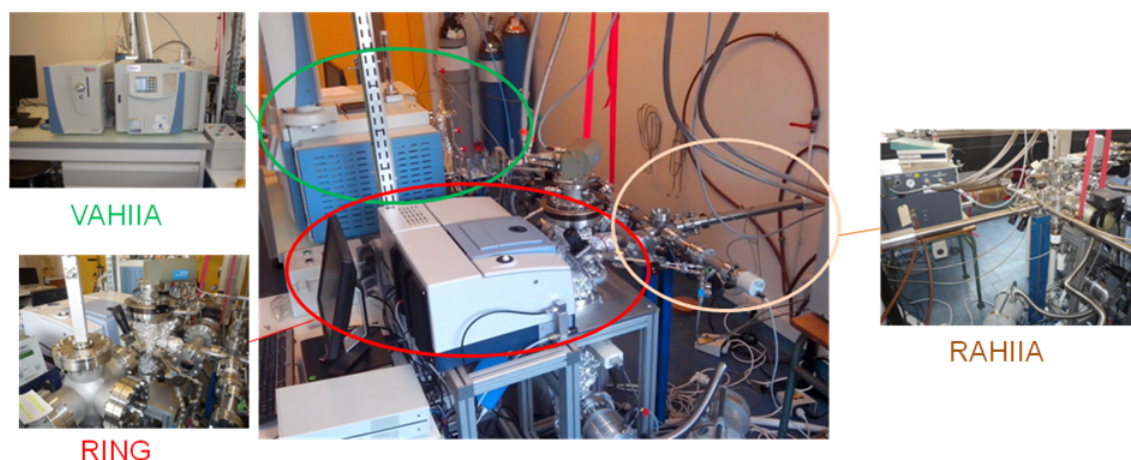


Figure 2: An overview of the AHIIA (Analysis from the Heating of Interstellar Ice analogs) device with the different parts used for the development of the three projects, RING, VAHIIA and RAHIIA.

### **3 The RING mechanistic approach: the example of the HMT and polyoxymethylene (POM) formation**

In the RING project, we determine the formation mechanism of key molecules that may be searched for in different environments using radiotelescopes, infrared telescopes or analytical instruments in space missions. HMT is a molecule of interest since it forms amino acids when acid-hydrolyzed (Hulett et al. 1971) but also it is often considered as an indicator of the photochemical processes (Bernstein et al. 1995). Indeed, after the VUV photolysis (44h) of an ice analog composed of  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$  and  $\text{NH}_3$ , in a ratio 3/1/1 at 78 K, which represents a temperature compatible for a grain at the edge of the disk, the formation of formaldehyde ( $\text{H}_2\text{CO}$ ) and carbon monoxide ( $\text{CO}$ ) is observed as well as  $\text{CO}_2$  and formic acid ( $\text{HCOOH}$ ) due to the water photodissociation (Öberg et al. 2009). After the sample heating up to 300 K, a residue is obtained. The infrared spectrum of this residue displays highly functionalized organic compounds mixture with few identified molecules such as HMT, a molecule displaying narrow and intense bands (Figure 3). Knowing that HMT is not produced if the mixture  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$  and  $\text{NH}_3$  is only heated at 300 K, it was suggested that HMT could be a tracer of photochemical processes. However, since the photoprocessing of an ice containing  $\text{CH}_3\text{OH}:\text{H}_2\text{O}:\text{NH}_3$  leads particularly to the formation of  $\text{CH}_2\text{O}$  and  $\text{HCOOH}$ , we investigated the possibility that HMT could be produced from a thermal process involving  $\text{H}_2\text{CO}$ ,  $\text{HCOOH}$  and  $\text{NH}_3$  molecules. By making deposits of bilayers of  $\text{H}_2\text{CO}/\text{NH}_3$  and  $\text{HCOOH}$ , in order to control the different stages of the reaction, we were able to isolate the various reaction intermediates and elucidate the HMT formation mechanism which is summarized in Figure 4 (Vinogradoff et al. 2011, 2012). In an environment dominated by water, if ammonia is two times more abundant than formaldehyde,  $\text{H}_2\text{CO}$  reacts with  $\text{NH}_3$  to produce aminomethanol ( $\text{NH}_2\text{CH}_2\text{OH}$ ) (Bossa et al. 2009). During the water desorption,  $\text{NH}_2\text{CH}_2\text{OH}$  is dehydrated into methanimine ( $\text{CH}_2\text{NH}$ ), a reaction which is catalyzed by  $\text{HCOOH}$ . Linear or ramified polymers of methanimine (PMI, polymethanimine) are then formed. The mechanism that leads to their formation is not well known yet. Other methanimine molecules can react with  $\text{HCOOH}$  leading to a cyclic compound in its salt form, the trimer of methaniminium formate ( $\text{TMT}^+$ ,  $\text{HCOO}^-$ ), TMT (TriMethyleneTriamine) being the first six member cycle that will lead to the HMT structure. This TMT salt is entrapped in the PMI matrix. This allows its persistence on the sample holder at a higher temperature than its own desorption temperature. Above 290 K a part of this salt decomposes leading to a release of methanimine that reacts with other TMT cycles forming HMT. PMI has also the ability to delay the HMT desorption. Indeed, pure HMT sublimates at 260 K while it desorbs at 400 K (Briani et al. 2013) in the presence of PMI. This fact is very valuable for HMT detection in cometary environments. These experiments demonstrate that HMT cannot be considered anymore as a tracer of photochemical processes, but that it can rather be considered as a tracer of thermal processing since it can be formed only from the warming of  $\text{H}_2\text{CO}$ ,  $\text{HCOOH}$  and  $\text{NH}_3$  ices.

The HMT formation is a good example to illustrate the increase of the molecular complexity after ice irradiation and warming, and it may be a good tracer of the initial composition of astrophysical ices (Vinogradoff et al. 2013). A change in the ammonia concentration in the mixture causes the formation of new products (Duvernay et al. 2014). In the case of  $\text{H}_2\text{O}:\text{NH}_3:\text{H}_2\text{CO}$  ice mixtures where  $\text{NH}_3$  is less abundant than  $\text{H}_2\text{CO}$  ( $0.2 < \text{NH}_3/\text{H}_2\text{CO} < 1$ ), a reaction occurs above 100 K between  $\text{H}_2\text{CO}$  and  $\text{H}_2\text{O}$ , catalyzed by  $\text{NH}_3$  giving the methylene glycol ( $\text{HOCH}_2\text{OH}$ ) that sublimates at 220 K. At very low  $\text{NH}_3$  concentration ( $\text{NH}_3/\text{H}_2\text{CO} < 0.03$ ) in a water-dominated ice, POM polymer is formed ( $\text{HO}-(\text{CH}_2\text{O})_n\text{-H}$ ) from direct self-polymerization of formaldehyde catalyzed by  $\text{NH}_3$  (Schutte et al. 1993a,b). In these conditions, the major part (90%) of POM sublimates between 210 and 250 K under short chains of polymer ( $\text{HO}-(\text{CH}_2\text{O})_n\text{-H}$ ,  $n < 5$ ) that do not decompose into formaldehyde before sublimating (Duvernay et al. 2014). Only a small fraction of POM correspond-

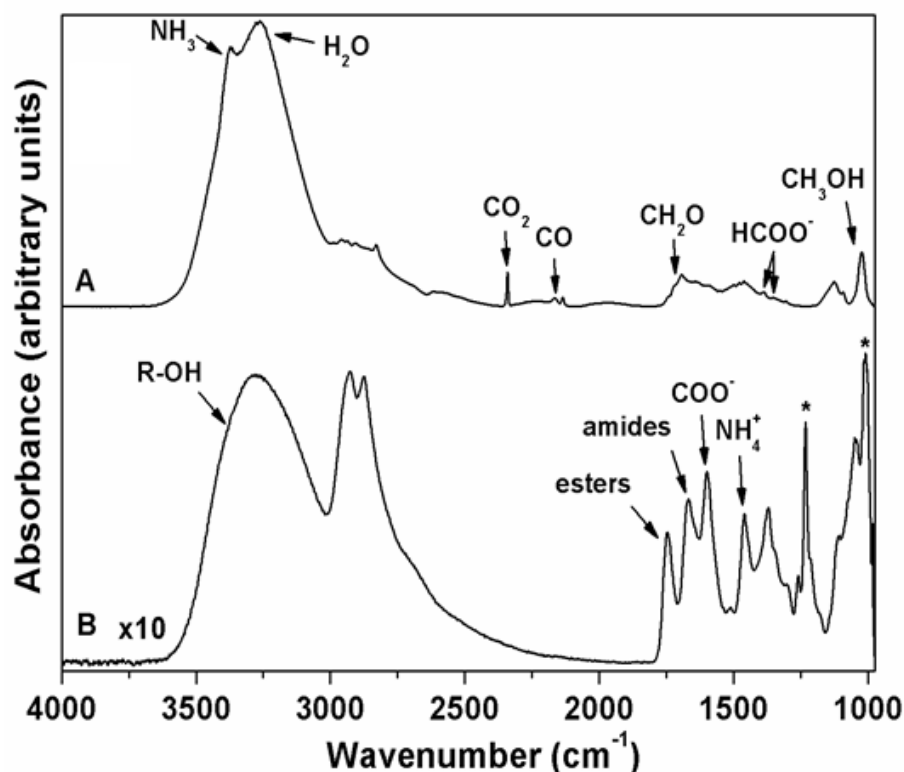


Figure 3: FT-IR spectrum of  $\text{CH}_3\text{OH}:\text{NH}_3:\text{H}_2\text{O}$  ice in a ratio 1:1:3 at 78 K, after 44h deposition and simultaneous VUV irradiation (spectrum A) and of the residue after warming to room temperature (spectrum B). \*Indicates the two main bands of HMT at  $1006\text{ cm}^{-1}$  (CN stretching) and  $1235\text{ cm}^{-1}$  (CN stretching).

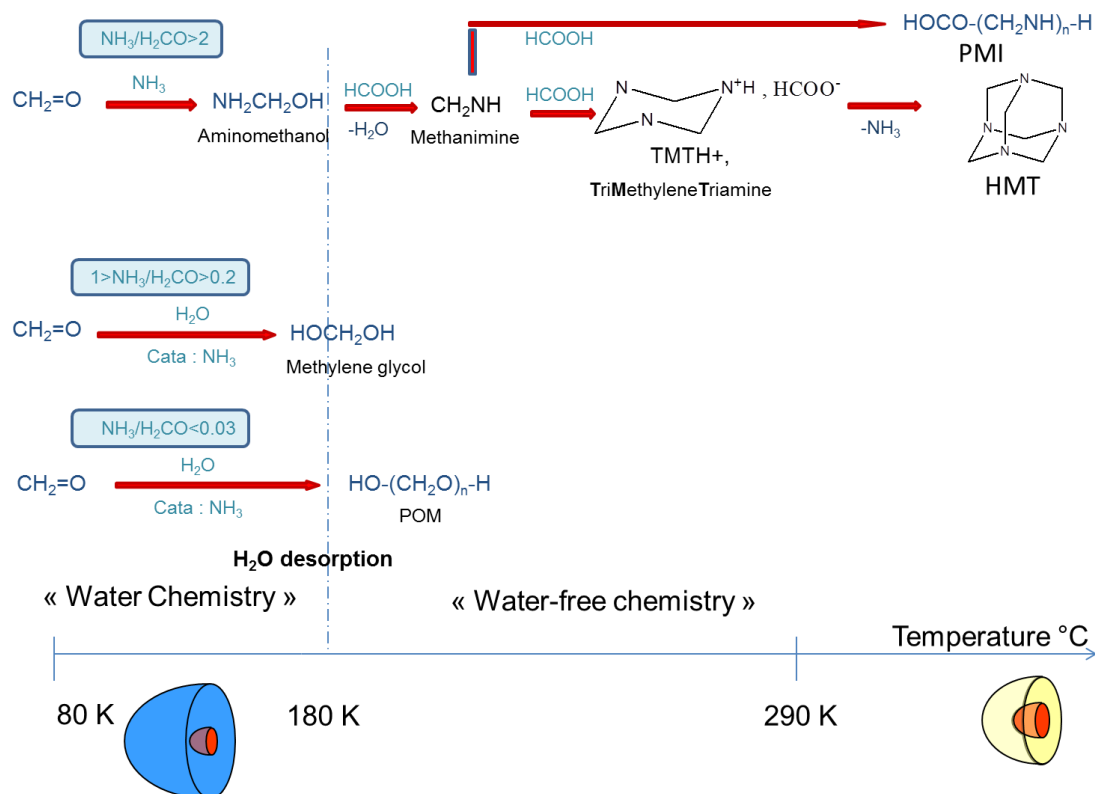


Figure 4: Chemical pathway leading to the HMT, methylene glycol and polymers (POM and PMI).

ing to the longer chain polymers decomposes into formaldehyde at a temperature higher than 250 K (Le Roy et al. 2012). We should note that the chain-length of volatile POM and their mass spectra obtained in our experiments are very different from commercial POM or synthesized POM (formed without water in the initial mixture) which are often taken as references to explain the  $\text{H}_2\text{CO}$  distributed source in comets (Cottin & Fray 2008).

Formation ranges of POM, methylene glycol and aminomethanol/HMT strongly depend on the initial ice composition of  $\text{NH}_3/\text{H}_2\text{CO}/\text{H}_2\text{O}$  (Figure 5). It follows that HMT and POM cannot be produced at the same time as the dominant products from the warming of an ice mixture containing  $\text{H}_2\text{O}$ ,  $\text{NH}_3$  and  $\text{H}_2\text{CO}$ . But if we rely on the abundance of  $\text{NH}_3$  and  $\text{H}_2\text{CO}$  in different YSOs objects and in cometary environments (Zasowski et al. 2009), we observe that  $\text{NH}_2\text{CH}_2\text{OH}$  and thereafter HMT would be preferentially formed (Duvernay et al. 2014). The detection of POM and HMT in the forthcoming Rosetta mission that plans to study cometary composition will thus strongly depend on the initial ice composition of the comet. Besides the elucidation of the mechanism and conditions of formation of the above cited key products, the mechanistic approach in the RING project allows a better evaluation of which tool to use during scientific missions to detect these products. For example, based on the experimental simulations just described, what is the best instrument to characterize POM and HMT in the forthcoming Rosetta mission? Three experiments based on mass spectrometry may allow their characterization. The COSAC instrument on board of the Philae lander dedicated to the study of cometary nucleus will involve indirect detection of these compounds because solid samples have to be heated to temperatures which can reach  $600^\circ\text{C}$ . At these temperatures POM decomposes into formaldehyde, and HMT may be formed without being initially present in the cometary nucleus and then decomposes into methanimine/ammonia. In the COSIMA instrument which will analyze dust grains emitted by the cometary nucleus, due to the temperature of the collected grains (253-303 K), HMT could be formed inside the instrument from precursors even if it is absent from the collected sample, while only the refractory POM representing a low fraction of the total POM should be observed (Le Roy et al. 2012). On board of the Rosetta orbiter, ROSINA which is designed to determine the composition of the cometary atmosphere and ionosphere, would be the best instrument for detecting HMT and POM. In this case, these products could be directly detected depending on the comet's relative position to the sun. However, it is important to underline that the detection of POM and aminomethanol (or HMT) by one of the instruments of the Rosetta mission would be a proof of the heterogeneity of the grain composition in the disk where they are assembled to form comets.

Moreover, competitive reactions to POM, PMI and HMT formation can occur if other molecules are present in the initial ice. For instance, if hydrogen cyanide (HCN) is present, the methanimine can react with  $\text{NH}_4^+-\text{CN}$  leading to the formation of aminoacetonitrile ( $\text{NH}_2\text{CH}_2\text{CN}$ ). The  $\text{NH}_2\text{CH}_2\text{OH}$  is also in competition with hydroxyacetonitrile ( $\text{HOCH}_2\text{CN}$ ) since  $\text{CH}_2\text{O}$  can directly react with  $\text{NH}_4^+-\text{CN}$ . Therefore, the hydroxynitrile/aminonitrile ratio depends on the initial ice composition and particularly on the amount of HCN, as we have observed with a  $\text{H}_2\text{O}/\text{H}_2\text{CO}/\text{NH}_3/\text{HCN}$  mixture (Danger et al. 2012). Hydroxynitriles and aminonitriles precursors may be detected in star forming regions or in cometary environments during the ice desorption of the grains. Furthermore, a fraction of these molecules may remain trapped in the residue. These molecules can form, by acidic hydrolysis, hydroxyl acids and amino acids which are observed in carbonaceous meteorites.

## **4 The VAHIA (Volatile Analysis from the Heating of Interstellar Ice Analogs) project**

The VAHIA project is supported by an ANR for young researchers (ANR Grant ANR-12-JS08-0001-01) and addresses the analysis of Volatile Organic Compounds (VOC) sublimating from complex ice



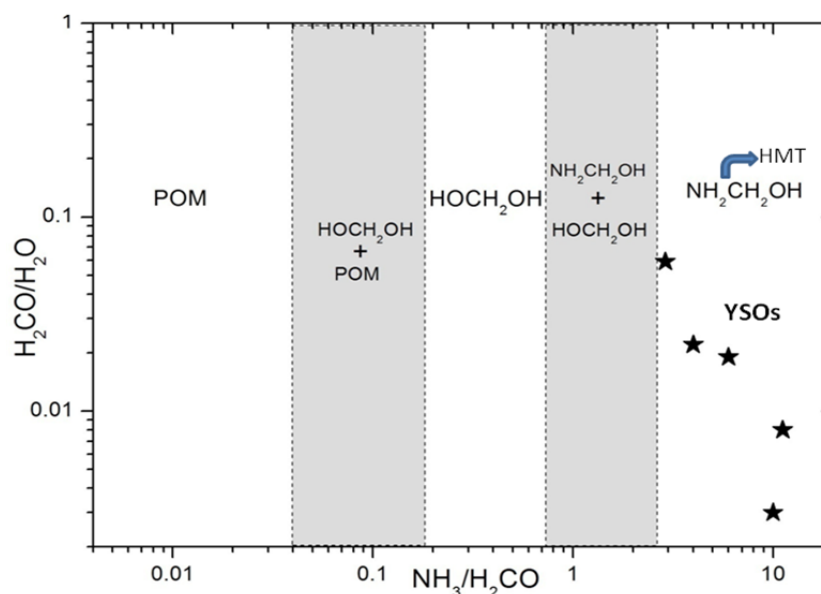


Figure 5: The different major products formed from the warming of the  $\text{H}_2\text{O}:\text{NH}_3:\text{H}_2\text{CO}$  ice mixtures as a function of the  $\text{NH}_3:\text{H}_2\text{CO}$  concentration and  $\text{H}_2\text{CO}:\text{H}_2\text{O}$  concentration ratios. Stars refer to the observed ice composition of several YSOs (adapted from Zasowski et al. 2009).

analogues when these latter are heated and/or irradiated. The characterization of sublimating species is of a crucial importance since they may take an important role in the formation and evolution of the organic refractory residues. Their monitoring will help understanding the complexity of the chemical reactivity occurring on the icy surface of interstellar and cometary dust grains, but also supporting data treatments of space mission such as Rosetta. To our knowledge, few studies reported the analysis of species sublimating in the vacuum chamber, and they were mainly target analysis (Cottin et al. 2000), and mostly used a quadrupole mass spectrometer to identify specific and expected compounds (Danger et al. 2014). However, and taking into account the potential importance of VOC in the understanding of chemical evolution of interstellar and cometary material, it may be very interesting to conduct a non-targeted screening of VOC using instruments capable of overcoming matrix effects and complexity. To fulfill VAHIA's objectives, we have developed an original experimental set-up that transfers online VOC sublimating from the vacuum chamber where the ice analogues are formed and processed to the GC-ion trap MS where they are analyzed (Abou Mrad et al. 2014). The heart of this set-up is an interface constituted of a preconcentration unit and a gaseous injection unit. This interface has two main roles: the first is to preconcentrate VOC sublimating from the chamber prior to their analysis and therefore overcoming the analytical sensitivity constraints induced by their slow desorption kinetics in the vacuum chamber, the second is to increase the preconcentrated sample pressure to facilitate its online transfer to the GC-MS instrument. The preconcentration unit is made of 6 pneumatic valves and a preconcentration loop. The scheme is to activate a particular set of valves to induce a differential pumping of compounds from the vacuum chamber ( $10^{-8}$  mbar) to the preconcentration loop submerged in liquid nitrogen. Compounds having sublimation temperature higher than 77 K will be trapped during an optimized period (14 h). The following step consists of warming the loop (pressure of a few mbar) and of adding helium into the loop to reach a total pressure between 100 and 300 mbar. The last step is the transfer of species from the preconcentration loop to the injection loop, the main constituent of the gaseous injection unit. This transfer is made possible due to the pressure differential between the preconcentration loop (100-300 mbar) and the injection loop (previously pumped to a few mbars). The injection loop determines a constant volume of gas to



be injected into the GC inlet.

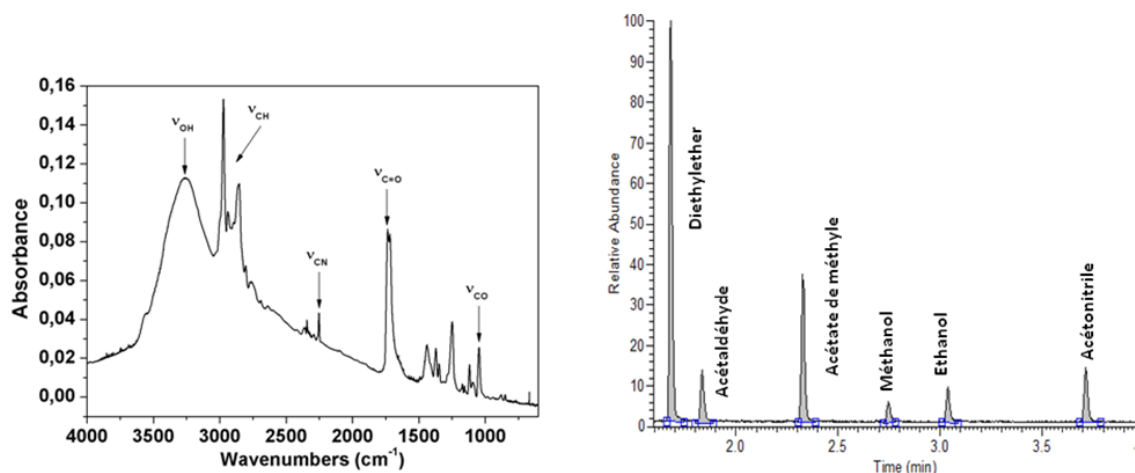


Figure 6: FT-IR spectrum of a mixture of 6 standards (diethyl ether, acetaldehyde, methyl acetate, methanol, ethanol and acetonitrile) (left); GC-MS chromatogram of the compounds sublimated from the same deposited mixture at 20 K (right).

The overall system has been calibrated and optimized to ensure the best analytical sensitivity using compounds present or likely to be present in cometary environments. We have determined the optimal preconcentration parameters (trapping period, loop volume), transfer parameters (volume of helium added, injection loop volume) and GC-MS analysis (column used, injector temperature, oven temperature program, ion source temperature). The optimized method has been validated (Abou Mrad et al. 2014) and method performance (repeatability, robustness, sensitivity) are very satisfactory for trace VOC analysis sublimating from ice analogs. As a first application of the VAHIA system, a mixture of six standards (diethylether, acetaldehyde, methylacetate, methanol, ethanol and acetonitrile) has been deposited in the vacuum chamber at 20 K and the ice formation was monitored using infrared spectroscopy (Figure 6). As shown in this figure, the different chemical functions of the compounds constituting the mixture are identified but it is impossible to identify compounds themselves. After ice warming to 300 K, sublimating species were pumped out of the chamber, preconcentrated for 14 h and transferred to the GC-MS. The GC allowed the separation of the six compounds (Figure 6), their detection even at very low sublimating quantities (nanomoles) and their mass spectrum allowed their unambiguous identification. These results are very encouraging for a non-targeted screening of VOC and trace level VOC sublimating from complex ice mixtures such as (H<sub>2</sub>O/CH<sub>3</sub>OH/H<sub>2</sub>CO/NH<sub>3</sub>/CO/CO<sub>2</sub>).

## 5 The RAHIA (Residue Analysis from the Heating of Interstellar Ice Analogs) project

The objective of the RAHIA project is to determine and understand the chemical evolution and the composition of organics in the residues in order to make a comparison with the organic matter contained in comets, asteroids and meteorites. The analysis of the cometary grains returned by the Stardust spacecraft revealed the presence of complex organic molecules as methylamine and glycine, the simplest amino acid (Elsila et al. 2009). But much more information is obtained from targeted analysis using gas or liquid chromatography coupled to mass spectrometry on the soluble organic matter (SOM) fraction extracted from carbon-rich carbonaceous chondrites. After aqueous and/or acidic treatment and/or derivatization procedures, specific molecules can be characterized. The analysis

performed on the Murchison meteorite (Glavin et al. 2006, Pizzarello 2006, Botta et al. 2007), one of the most studied meteorites, revealed a varied and complex suites of organic molecules with more than 500 structures so far (Pizzarello 2006). Among them, carboxylic acids, sugars, nucleobases and amino acids have a major interest as sources of prebiotic organic material delivered to the early Earth by such objects and needed for the origin of life. Non-targeted analyses have been performed on Murchison SOM with VHRMS using FTICR-MS for identifying as much molecules as possible without any chemical treatments. This analysis revealed the presence of few thousands of different molecular compositions and likely millions of diverse structures (Schmitt-Kopplin et al. 2010). By considering exact masses, an elemental formula has been assigned for this SOM fraction:  $C_{100}H_{155}O_{20}N_3S_3$ . This latter shows a higher aliphaticity and oxygen content compared to the Murchison IOM fraction. All these data on meteorite analysis are valuable for comparison with experimental simulations in the laboratory. To determine the composition of the SOM extracted from our residue analog coming from the irradiation and warming of the previous ice analog ( $H_2O/CH_3OH/NH_3$ ), targeted analyses are currently performed by using GC-MS, HPLC-MS, and/or low resolution mass spectrometry. These analyses reveal before or after acid hydrolysis of the initial residue, the identification of various amino acids as well as di-amino acids (Munoz Caro et al. 2002, Nuevo et al. 2007, Nuevo et al. 2008, De Marcellus et al. 2011, Meinert et al. 2012). They also confirm the large amount of HMT, and the implication of the initial ice composition on its formation. In our studies, we performed non-targeted analysis by using VHRMS with a LTQ-orbitrap-XL instrument (collaboration with Roland Thissen et al., IPAG) on residues resulting from a VUV irradiation at 78 K of an ice containing  $H_2O/CH_3OH/NH_3$  in a ratio 3/1/1 and subsequently warmed to room temperature (Danger et al. 2013). After the SOM recovery in methanol, the molecule ionization is performed using electrospray ionization (ESI) source in the positive or negative mode providing a smooth ionization of molecules, limiting their fragmentations, which allows the identification of molecular ions with  $[M+H]^+$  or  $[M-H]^-$ , respectively. The advantages of this technique rely on the high resolution ( $R=100000$ ), the high sensitivity, the excellent mass accuracy and the ability to perform a MS/MS analysis on a selected ion. The overall spectra recorded in two different mass ranges (Figure 7) show that residues are constituted of an important molecular diversity with molecules having molecular masses beyond 4.000 Da. Among the detected molecules, specific molecules such as HMT and some of its derivatives were confirmed by MS/MS analyses.

By reporting all the ionic signals on the MDvEM diagram (Mass Defect versus Exact Mass), a trend line with repetitive pattern of formula  $(C_cH_hO_oN_n)$  emerges for the synthesized residue (green line in Figure 7). From the slope of this trend line, we determine an average elemental composition which translates that the carbon ( $H/C=1.6$ ,  $N/C=0.4$ ,  $O/C=0.4$ ) can be directly compared to meteoritic samples. The ratios  $O/C$  and  $N/C$  are equal in the residue whereas in the initial ice there are 4 times more O than N. This implies that N is efficiently incorporated during the residue synthesis, whereas an important loss of O occurs during the residue synthesis for instance through the desorption of secondary species such as  $H_2O$ ,  $CO$  or  $CO_2$ . Compared to the Murchison meteorite ( $H/C=1.55$ ,  $N/C=0.03$ ,  $O/C=0.2$ ), a good agreement is observed on the  $H/C$  ratio but differences are observed on the  $N/C$  ratio that may be explained in part by the initial composition of our ice which contains at least 5 times more ammonia than the proportion observed in astrophysical environments (17%). Furthermore, using  $^{12}C$  and  $^{13}C$  experiments as well as comparison to blank experiments, we were able to discriminate ionic signals coming from the residue synthesis and from the residue contamination. Thus, we definitely demonstrated that the molecular complexity observed comes from the residue synthesis and not from contamination.

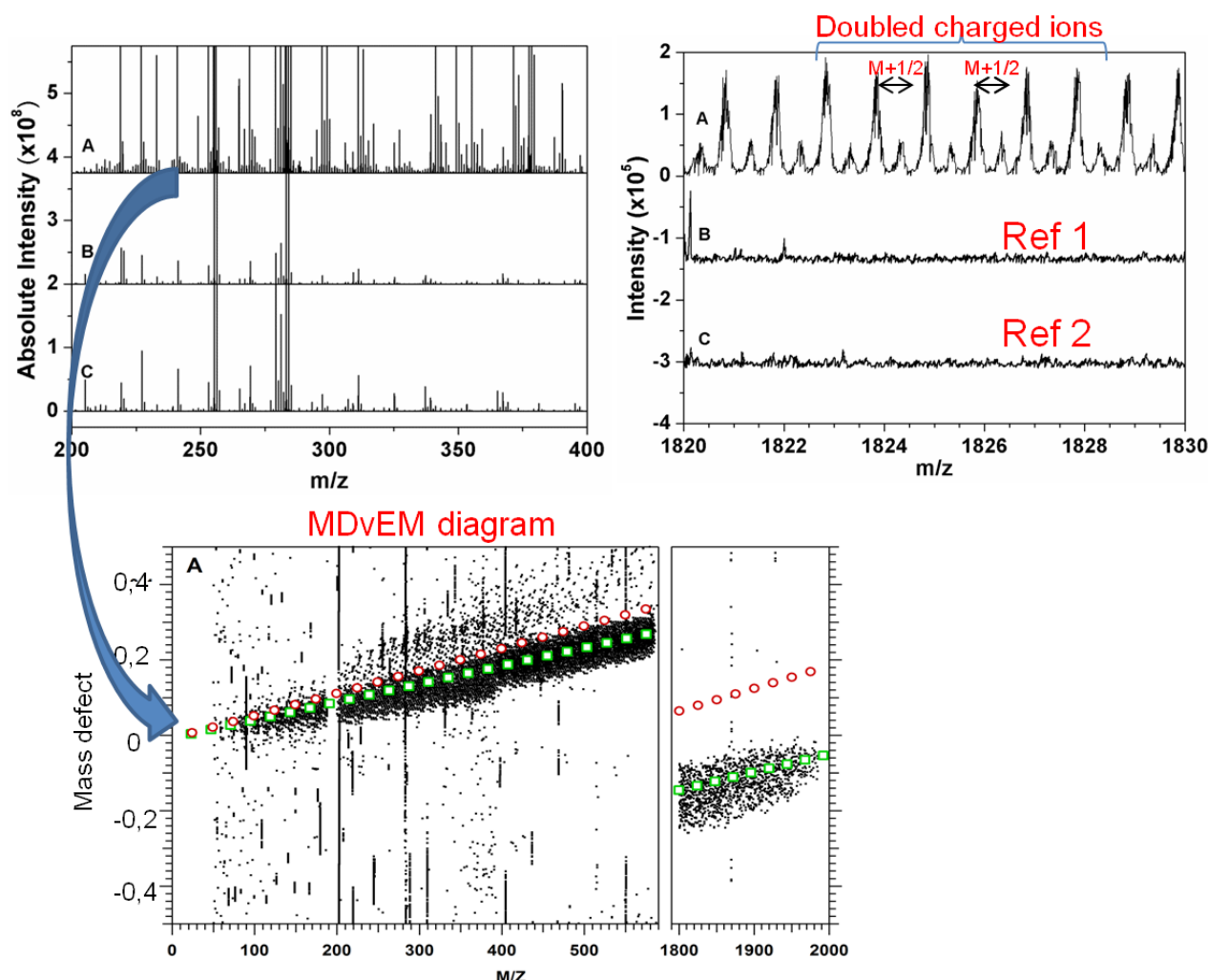


Figure 7: The top of the figure displays FT-orbitrap SIM spectra obtained in ESI negative mode for the  $m/z$  range 200-400 and 1820-1830 after recovery in methanol of (A) a refractory residue formed from an ice mixture containing  $^{12}\text{CH}_3\text{OH}:\text{NH}_3:\text{H}_2\text{O}$  (1:1:3), (B-REF1) a blank coming from an ice mixture deposited on the  $\text{MgF}_2$  window and warmed without VUV irradiation, and (C-REF2) a blank coming from a VUV irradiation of the  $\text{MgF}_2$  window, without gas mixture deposit. For blanks and sample formation, all the different steps are exactly the same. The bottom of the figure displays a MDvEM diagram corresponding to mass spectra of (A) the  $^{12}\text{C}$  residue analyzed in the negative ESI mode. The green squares represent a simulated slope of hypothetical repetitive pattern containing  $^{12}\text{C}$  of formula  $(\text{C}_c\text{H}_h\text{O}_o\text{N}_n)$  for the residue synthesis, while the red circles refer to the average slope of the same pattern containing  $^{13}\text{C}$ .

## 6 Conclusions

The simulation experiments in the laboratory on ice analogs are fundamental to understand the origin of the observed molecules in various astrophysical objects (disks, comets and meteorites) and to provide new molecules to search for in cometary and interstellar environments. The mechanistic approach developed in the RING project allowed us to explain the synthesis of various organic molecules in the grains and we elaborated a chemical reaction network starting from the primitive ice constituents (Theulé et al. 2013). Thermal reactions are not limited only to radical recombination but also include reactions between neutral species in the icy grains. Thermal and Photochemical reactions contribute to the increase of the molecular complexity and diversity. All data (activation barrier and desorption energy) collected are useful to determine the conditions of observation of molecules in various astrophysical objects. The results obtained in the VAHIA project are promising and they would assist in data processing collected in space missions (Rosetta). The molecules sublimating from the ice mantle would be precursors of the formation of refractory compounds. In the RAHIA global approach, we use ultra-high resolution mass spectrometry with an LTQ-orbitrap-XL instrument to determine the stoichiometric composition of the residue and the influence of the alteration processes (aqueous treatment, thermolysis, photolysis) which can change the organic matter composition in parent bodies of meteorites. The data treatment issued from the spectral analysis can be useful to understand the chemical history of the interstellar organic matter.

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