## Cometary organic chemistry: understanding the history of their ice from their composition, and potential astrobiology interest

Hervé Cottin, Yves Bénilan, Nicolas Fray, Marie-Claire Gazeau, François Raulin, Robert Sternberg

> LISA - Laboratoire Interuniversitaire des Systèmes Atmosphériques Universités Paris 12 - Paris 7, CNRS UMR 7583

### cottin@lisa.univ-paris12.fr

#### Introduction

To date, about twenty five molecules have been detected in the gaseous phase of comets. But so far, we do not have any direct measurement of the nucleus composition.

For more than twenty years, many laboratory experiments are devoted to the study of the chemistry of cometary and interstellar ices. All of them tend to indicate that compounds more complex than those already detected are also very likely to be present: high molecular weight molecules, polymers, amino acids precursors, or even amino acids themselves. Thus, comets are of prime interest for astrobiology studies.

The aim of this short review is to present the different kind of laboratory experiments implemented so far and to build an inventory of organic molecules detected. Doing so, it is interesting to address the following questions:

1) Are some of these complex compounds a key to understand the history of cometary ices? A molecule could be a signature of such or such process, prevailing during the history of a comet: thermal process, photolysis, charged particles, catalysis with grains.

2) What is the astrobiological significance of such compounds?

3) Will those molecules be detected during Rosetta mission?

4) Can we already infer the presence of those complex organics through the observation of extended sources such as  $\rm H_2CO$  ?

### 1 - Observations and laboratory simulations

Only volatile molecules (Table 1) have been detected so far in cometary atmospheres (comae), as no direct cometary sample has ever been analyzed. For a better insight into more complex, less volatile material, one has to turn to experimental laboratory work. The principle of such experiments is the following: from observations of the most abundant species in comae and in the interstellar medium, one can infer the probable composition of the nucleus ices. A gaseous sample of the key species is deposited under vacuum on a cold substrate and irradiated during or after deposition by UV photons or charged particles. Condensed ices are sometimes simply warmed up slowly without irradiation. When the sample is warmed up for analysis a refractory organic residue remains on the substrate as the volatiles sublimate (Figure 1). Greenberg has called this residue Yellow Stuff. Bernstein, Allamandola, and Sandford, (1997) have shown that the organic residue is formed only

when the initial mixture of ices contains polar molecules such as CH<sub>3</sub>OH and NH<sub>3</sub>.

The diversity of organic compounds synthesized is remarkable but their identification is seldom exhaustive. Table 2 is a simplified list of all the detected compounds. The simplest compounds such as CO, CO<sub>2</sub>, H<sub>2</sub>CO and CH<sub>4</sub> are detected in almost all the experiments, if the irradiated ice contains the appropriate elements. For more complex molecules, it depends on the ice composition and the nature of the energy source.

In addition to chemical transformations, it must be mentioned that experiments on the trapping of gases during ice condensation suggest that these processes play an important role in determining the composition of the ice and could lead to important enrichment or depletion between the gaseous and solid phases (Notesco and Bar-Nun, 1996; Notesco and Bar-Nun, 1997; Notesco, Laufer, and Bar-Nun, 1997).

	Abundance		Abundance
Compound	In comet	Compound	In comet
	Hale-Bopp		Hale-Bopp
	(H <sub>2</sub> 0=100)		(H <sub>2</sub> 0=100)
H <sub>2</sub> O	100	HCN	0.25
СО	23	HNCO	0.10
CO <sub>2</sub>	6	HNC	0.04
CH <sub>4</sub>	0.6	CH <sub>3</sub> CN	0.02
$C_2H_6$	0.6	HC <sub>3</sub> N	0.02
$C_2H_2$	0.2	NH <sub>2</sub> CHO	0.015
CH <sub>3</sub> OH	2.4	$H_2S$	1.5
H <sub>2</sub> CO	1.1	OCS	0.4
CH <sub>2</sub> OHCH <sub>2</sub> OH	0.25	SO	0.3
нсоон	0.09	SO <sub>2</sub>	0.2
HCOOCH <sub>3</sub>	0.08	H <sub>2</sub> CS	0.02
CH <sub>3</sub> CHO	0.025	$S_2$	0.005 (Hya)
NH <sub>3</sub>	0.7		

 Table 1 : Molecules detected in the coma of comet Hale-Bopp (or Hyakutake if mentioned) (adapted from Despois et al (2002))



**Figure 1:** A typical experimental setup allowing the irradiation (by UV and/or energetic protons) of cometary ice analogs made by deposition of a gas mixture on a rotating aluminum mirror cooled down to 10 K in a cryostat. The ice evolution can be analysed in situ by infrared reflection spectroscopy, and the volatiles released during warming, by mass spectrometry. The room temperature residue can be collected for further analysis such as GC-MS (Gas Chromatography coupled to Mass Spectrometry ), HPLC (High Performance Liquid Chromatography) and many other. From Hudson and Moore (1999).



**Table 2**: Molecules detected during experimental simulations of cometary ice analogs. Italic letters refer to molecules actually detected in comets. (t) means tentative detection only in the analogs. Amino acids (alanine, AIB, ... except glycine) were detected after acid hydrolysis of the room temperature residue. Updated from Cottin *et al.* 1999.

# 2. Energy deposition during laboratory simulations

Three kinds of energetic processing occur on icy coated dust grains in interstellar clouds (potentially precometary ices – see Sect. 5) or in the outer layers of comet ices in the Solar system:

In interstellar clouds, icy coated dust particles are subjected to processing by:

- <u>Charged particles</u>: Galactic cosmic rays.
- <u>UV-photons</u>: Lyman  $\alpha$  photons from neighboring stars (in the diffuse outer regions of a cloud), or UV-photons induced by galactic cosmic rays (in the inner regions of dense clouds).
- <u>*Thermal processes*</u>: Cycling between the cold center of a dense cloud and its warmer diffuse outer regions.

In the Solar system, the outer layers of comets undergo the same processes:

- *Charged particles*: Galactic cosmic rays, mainly in the Kuiper belt and the Oort cloud. This process has the largest effect on the outer few meters of the nucleus.
- *UV-photons*: Solar-UV, mainly in the inner Solar system when the comet is close to the Sun. This process would affect the outer few micrometers of the nucleus. Also during the Solar system formation, in the

external layers of the disk, when solar UV luminosity was much higher than today.

• *Thermal processes*: During the formation of the Solar System (depending on the region in which the comet accretes), and in the inner Solar System (when the comet approaches perihelion).

Due to the diversity of environments involved, constraining the degrees to which different processes affect cosmic ices is a highly convoluted problem. Differences between the products synthesized during processing, according to the energy sources, could give information on the history of cometary matter and comets. Investigations are in progress to address this question.

## 2.1 UV Irradiation

UV irradiation is performed using a flowing hydrogen discharge lamp (powered by a microwave cavity) delivering mainly Lyman  $\alpha$  photons (122nm) and a broad band of photons centered at 160 nm (see Allamandola, Sandford, and Valero, (1988) for a detailed description). The irradiated ices comprise common cometary small molecules but the initial abundances of CH<sub>3</sub>OH, NH<sub>3</sub> and/or CO relative to H<sub>2</sub>O are usually higher than those deduced for present-day comets and displayed in Table 1. During these experiments a wide variety of organic compounds have been

identified. From an initial mix of  $H_2O$  : CO :  $NH_3$  (Ratio = 5 : 5 : 1), glycine, the simplest amino acid, acetamide, glyceramide, and many other molecules have been detected by GC-MS (Briggs et al., 1992). Analysis by MS-MS on the organic residues formed, leads to the detection of heavier compounds: several cyclic molecules and PAHs (Greenberg and Mendoza-Gomez, 1993). The composition of the heaviest part of the residue is still unknown but an elemental composition based on the over-all structure of the mass spectra is given by Greenberg and Li, (1998) (C : O : N : H = 1 : 0.06 : >0.001 : 1.1).

Among the molecules synthesized after such irradiations of ices, one of them is of great interest. Bernstein et al. (1995) have identified abundant Hexamethylenetetramine (HMT –  $C_6H_{12}N_4$ ) in the refractory residue. This compound has exobiological implications since its acid hydrolysis products are amino-acids (Wolman et al., 1971). Typically, for an initial composition of  $H_2O$  :  $CH_3OH$  : CO :  $NH_3$  (10 : 5 : 1 : 1), the organic residue at 300 K contains HMT (~ 60 %), ethers and POM-like polymers (~ 20 %), ketones and amides (~ 20 %). 1/5 of the carbon and 1/2 of the nitrogen from the initial ice composition remain in the refractory part (Bernstein et al., 1995). Thus a large fraction of HMT is formed (60 % of the residue) whereas only 5 % NH<sub>3</sub> is present in the ice before irradiation. A scheme of HMT production is shown in Fig. 2. Formaldehyde is produced by methanol UV oxidation. It then reacts with ammonia to produce methylimine and its trimer : hexahydro-1,3,5-triazine. Successive reactions with formaldehyde and ammonia result in the formation of HMT (Bernstein et al., 1995). Methanol plays a key role and it has been shown by <sup>13</sup>C isotopic substitution that it is the source of HMT's carbon. The production of HMT and some HMT family molecules has been studied in great details by (Muñoz Caro, 2003).



Figure 2: Hexamethylene Tetramine (HMT) Chemistry. From (Bernstein et al., 1995).

Bernstein et al., (2002) and Muñoz Caro et al., (2002) have detected a great number of amino acids (such as glycine, alanine, sarcosine, valine, proline, serine etc...) in residues obtained after UV irradiation of ice mixtures made of H<sub>2</sub>O: NH<sub>3</sub>: CH<sub>3</sub>OH: HCN and H<sub>2</sub>O: CH<sub>3</sub>OH: NH<sub>3</sub>: CO: CO<sub>2</sub>, respectively. Unhydrolyzed residues produce only a trace of glycine whose detection has already been reported by (Briggs et al., 1992) without any liquid water introduced to the analysis protocol. The detection of the other amino acids requires an acid hydrolysis of the residue in very strong conditions (HCl  $\ge$  6 M and T  $\ge$  100 °C). Therefore it is not clear to date if 1) amino acids are present themselves in the laboratory residues, and henceforth in cometary ices, or if "only" amino acids precursors are synthesized, and 2) if the residues' processing (acid hydrolysis) is relevant to any chemistry which could have turned the amino acids' precursors imported by cometary impacts in the primitive oceans of the early Earth into actual amino acids.

#### 2.2 Irradiation by charged particles

Important work concerning the particle bombardment of ices has been performed by Strazzulla's team in Catania and in Marla Moore's laboratory at NASA Goddard Space Flight Center. The particles used are H<sup>+</sup>, He<sup>+</sup>, N<sup>+</sup> or Ar. The bombardment of a large diversity of carboncontaining ices induces an evolution toward an amorphous material called by Strazzulla *Ion Produced Hydrogenated Amorphous Carbon* (IPHAC) (Strazzulla, 1997; Strazzulla and Baratta, 1991; Strazzulla et al., 1991).

The general results are the following : up to a dose of about 10 eV/C-atom the ice is partially converted into a refractory material. From 10 to 25 eV/C-atom, a massive loss of H is observed and the target evolves to an organic material made of

chemical chains of different sizes. For stronger irradiations ( $\geq 25$  eV/C-atom) IPHAC, the ultimate state of organic degradation, is formed (Strazzulla, 1997). It has been shown by (Jenniskens et al., 1993) that energetic UV (10 eV) irradiation of the organic residue of processed ices also leads to IPHAC formation, which then can be also called : *Irradiation Produced Hydrogenated Amorphous Carbon*. Thus, after a typical lifetime in the interstellar medium, UV radiation and/or particles convert the organic mantle of interstellar dust into amorphous hydrogenated carbon.

A set of data comparing UV photolysis and ion irradiation of ices showed that the yield of major products was similar for a simple ice containing H<sub>2</sub>O and CO<sub>2</sub> (Gerakines, Moore, and Hudson, 2000), showing that the ice chemistry seems to be quite similar whether induced by photons or charged particles. Indeed, HMT production has been reported when interstellar ice analogs containing CH<sub>3</sub>OH and NH<sub>3</sub> are irradiated with protons (Cottin, Szopa, and Moore, 2001), the same as with photons. The main difference is that UV photons (typically at 122 nm) only affect a few tenths of a micron in water dominated ice, whereas protons can reach and alter the ice composition down to a few meters depth.

Chemical differentiation is more noticeable when molecules not dissociated by photons with a wavelength of 122 nm and above are involved in the chemical processes. This is the case for CO and N<sub>2</sub>. Different results are obtained if pure CO is photolyzed or proton irradiated (Gerakines and Moore, 2001). Likewise N<sub>3</sub><sup>+</sup> is detected when ices containing N<sub>2</sub> are proton irradiated, but not after photolysis (Hudson and Moore, 2002). It seems that it is more the energy level than the way it is deposited (UV or charged particles) that matters for chemistry.

Kobayashi et al., (1995) and Kasamatsu et al. (1997) were the first to report amino acid production from irradiated ices. After an irradiation by 3 MeV protons of mixtures containing water, ammonia and a carbon-containing molecule (carbon monoxide, methane or propane), they detected by HPLC several amino acids : glycine, and for the first time in a cometary simulation, alanine, aminobutiric acid and aminoisobutiric acid. These new detections were not made directly from the organic residue, but after an acid-hydrolysis in water. Likewise for UV irradiation, only traces of glycine were found during the analysis of unhydrolyzed residues.

## 2.3 Thermal processing of ices

Polyoxymethylene and associated molecules and polymers have been detected when several mixtures containing formaldehyde, instead of being irradiated, were warmed slowly to room temperature (Schutte, Allamandola, and Sandford, 1993a; Schutte, Allamandola, and Sandford, 1993b).

There are many differences between the organics detected with or without UV processing of ices. Without irradiation, HMT is not detected, which is quite surprising as H<sub>2</sub>CO and NH<sub>3</sub> readily react in the gaseous phase to form HMT (Bernstein et al., 1995; Walker, 1964). Likewise, ketones, amides or esters, easily synthesized under irradiation, are quite rare in those thermal experiments. It seems that UV photons provide enough energy to surmount the energy barrier for formation of these molecules. Without UV, POM's production is favored since it requires less energy.

## 2.4 Relevance and importance of laboratory simulations

Of course, an irradiation of a few hours can not reproduce millions of years or more of slow evolution with complex heterogeneous chemistry in an interstellar environment that will never be completely reproduced in the laboratory. Nevertheless, in the 3.4 µm region, infrared spectra of methane and butane mixtures after a particle irradiation present a very good fit with the observations of dust particles in the diffuse interstellar medium (i.e. highly processed material), and even with spectra of residues from the Murchinson meteorite (Pendleton et al., 1994). The same results have been obtained with residues of  $H_2O$ : CO: NH<sub>3</sub>: CH<sub>4</sub>/C<sub>2</sub>H<sub>2</sub>/CH<sub>3</sub>OH, which have been exposed to direct solar UV radiation on the EURECA space station (Greenberg and Li, 1997; Greenberg et al., 1995). These are also highly processed materials. Thus Strazzulla's IPHAC appears to be similar to the refractory mantle of dust grains in the harsh conditions of the diffuse interstellar medium. The less processed mantle formed in molecular clouds is almost certainly composed of the large range of molecules detected after experimental simulations, and the abundances of characteristic molecules like HMT or POM depends on the history of the grain and the relative contribution of the different energy sources : UV and proton irradiation lead to HMT, thermal processing to POM-like polymers. A very simplified view of these conclusions could be to consider that comets which were accreted in the Jupiter/Saturn area would have experienced more thermal processing than those accreted beyond the orbit of Neptune, which might have kept an interstellar composition with an history dominated by photons and protons irradiation (Figure 3) Importance of such simulations is underlined if one consider that data drawn from these simulations are necessary for the preparation of space missions to comets. A good illustration of this point is the selection and calibration of chromatographic columns for the COSAC experiment (ROSETTA

mission - ESA) that requires an anticipation of the nature of the molecules to be searched for.



#### A link between comets composition and the ice history ?

**Figure 3**: Simplified view of a potential link between the composition of the refractory component of cometary organics and the accretion region of the comet.

#### 3. Comets and Astrobiology

It is now quite obvious that comets are important reservoirs of a wide variety of organic compounds :

- From groundbased observations, leading to the detection of more than twenty stable small molecules ;
- From in situ measurements by the Vega and Giotto Spacecrafts, which detected large molecules in dust grains by mass spectroscopy;
- From laboratory simulations of irradiated ices with composition relevant to the interstellar medium or to comets. They lead to the formation of a complex refractory organic mantle

Five families of compounds are considered to be the key prebiotic monomers required before starting a chemical evolution from which life would arise. These are amino-acids, purine bases (adenine and guanine), pyrimidines bases (cytosine, uracil and thymine), sugars and fatty acids. It is very interesting to note, that even if these compounds have not been detected in comets (maybe because of limitations in the sensitivity of telescopes, but also essentially because the synthesis of most of them requires liquid water), they can easily be produced in an early Earth environment from cometary precursors such as HCN, HC<sub>3</sub>N, HCHO and CO which have been firmly detected in cometary comae (Table 3).



Table 3: Prebiotic syntheses from cometary molecules From (Oro and Cosmovici, 1997)

The other elements required, according to Table 3, for a protocell formation, are also present on comets. Phosphorus, which is involved in the synthesis of sugars, has been detected by mass spectroscopy (m/e = 31) in grains of comet Halley by the PUMA mass spectrometer on board Vega 1. But its abundance is very low and detection may have been affected by interference from ions such CH<sub>2</sub>OH<sup>+</sup> (Kissel and Krueger, 1987). However, analysis by laser probe mass spectroscopy of interplanetary dust particles (IDPs), whose cometary origin is probable, has led to the detection of PO2 and PO3 anions (Radicati-Di-Brozolo, Bunch, and Chang, 1986). Ni and Fe have been detected in comet Ikeya-Seki and Halley (see (Crovisier, 1997) for a recent review).

Nevertheless, complex compounds of exobiological interest may also be present in comets. The only detection of adenine is a very tentative interpretation of PUMA's mass spectra of comet Halley's dust (Kissel and Krueger, 1987). Such a molecule could be synthesized by HCN condensation without any liquid water (Oro and Cosmovici, 1997; Wakamutsu et al., 1966). As already stated earlier in this paper Bernstein et al., (2002) and Muñoz Caro et al., (2002) have detected a great number of amino acids (such as glycine, alanine, sarcosine, valine, proline, serine etc...) in residues obtained after UV irradiation of ice mixtures made of H2O: NH3: CH3OH: HCN and H<sub>2</sub>O: CH<sub>3</sub>OH: NH<sub>3</sub>: CO: CO<sub>2</sub> respectively. But the detection of amino acids other than glycine requires an acid hydrolysis of the residue in very strong conditions (HCl  $\ge$  6 M and T  $\ge$  100 °C).

Thus, comets may have imported prebiotic elements to early Earth, which, when mixed with liquid water, have allowed the synthesis of all molecules thought to be necessary for the origin of life. To date, it is not clear as for either the importation of such key compounds occurs at the simple stage of HCN, HC<sub>3</sub>N, HCHO..., or more elaborated species such as amino acids, puric and pyrimidic acids and others, but one can say for sure that comets are of prime interest to understand the origin of life. But before seeding the oceans, those compounds have to survive:

• if brought by small dust particles, they are subject in the interplanetary medium to the action of solar UV radiation, solar wind particles and galactic cosmic rays; while the particle comet is slowed down and warmed up by the Earth's atmosphere, they must resist to pyrolysis (destruction at very high temperature). If they reach the ground, they should also resist to the ensuing impact.

• alternatively, if the nucleus impacts directly the Earth, can the molecule survive the dramatic energy release?

Experiments conducted in space have shown that amino acids are quite unstable to solar UVs, but also that when they are somehow shielded in minerals, such as meteoritic powder, they can survive in space, and undergo no racemization (Barbier et al., 2002; Boillot et al., 2002).

The case of of impacts of large bodies has been theoretically treated by (Chyba et al., 1990). It appears that organic compounds (even amino acids, if present) contained in cometary impactors of 100 to 200 m in size could survive a collision with Earth in a 10 bar CO<sub>2</sub> atmosphere thanks to an efficient aerobreaking. Comparisons with Venus and Mars lead us to think that it is the most probable composition of the primitive atmosphere. On the experimental part, (Blank et al., 2001) conducted a series of shock experiments to assess the feasibility of the delivery of amino acids to the Earth via cometary impacts. It appears that a large fraction of the amino acids do survive impacts. It has also been shown that some chemistry occurs, which leads to the formation of peptide bonds and new compounds including amino acid dimers.

## 4. In Situ analysis of a cometary nucleus : The Rosetta mission

In the Solar System, several major space missions relate to comets. ESA ROSETTA probe will reach comet 69P/Churyumov-Gerasimenko after a ten year cruise in 2014. It will meet the comet and follow it during almost two years, during which a lander will be deposited on the surface. But are the most crucial compounds mentioned in this paper going to be detected with ROSETTA instruments ? For instance, if one refers to HMT already mentioned in this paper, its detection in the IR would be masked by the Si-O and C-O vibration bands that are in the same region as the strongest HMT infrared signatures.



Figure 4: HMT injected into one of the columns selected for the Rosetta mission, along with other compounds expected to be present on the cometary nucleus (including : benzene, toluene, pyridine, octane, nonane, decane, pentanol, xylene, naphtalene, indene, trioxane). (Cottin, Szopa, and Moore, 2001)

On the lander, the COSAC experiment will perform a chemical analysis of cometary volatiles by gas chromatography of samples taken after drilling down to 20 cm below the surface. With a detection limit of  $10^{-5}$ - $10^{-6}$  with respect to water, more than 100 cometary species might be detected (Szopa et al., 2003). The use of chiral colums will allow the measurement of enantiomeric excess if any. Direct detection of HMT should be feasible by in situ measurements with the GC-MS on board the lander of the Rosetta mission (Figure 4). But the case of POM detection is still unclear and a direct detection of the polymer remains uncertain.

## 5. Refractory organics as an origin for cometary extended sources

But before ROSETTA results, which are 10 years from now, is there any chance we could already infer the presence of complex organics through the observation of extended sources such as  $H_2CO$ ?

The distribution of formaldehyde in comet Halley, as reported in (Meier et al., 1993), has not been satisfactorily explained, either as a parent molecule released from the nucleus, or as a daughter product of any known parent gaseous cometary compound. Based on in-situ measurements and laboratory work on cometary ice analogs presented here above, it is now established that cometary grains are probably composed of a mixture of inorganic (silicates) and organic (high molecular weight molecules) material. Henceforth it is likely that refractory organic molecules can be slowly degraded by solar UV photons and/or heat and that they release volatile fragments in the coma.

Based on quantitative measurements of the production of formaldehyde from polyoxyméthylène by thermaland photodegradation, it has been shown that the degradation of this polymer is to date the best interpretation for formaldehyde measurements in comet Halley. Because of the large number of uncertain parameters (mostly grains distribution and temperature) one cannot derive a sharp estimate of the amount of POM on cometary grains. Nevertheless a nominal value of about 3 to 4 % in mass of POM on grains, and a related mixing ratio for parent formaldehyde of a few tenths of a percent relative to water allow a good agreement between modeling and observations (Figure 5) (Cottin et al., 2004; Cottin et al., 2001). Both nominal values are quite realistic if one refers to previous estimates based on observations and laboratory work (Bernstein et al., 1995; Bockelée-Morvan et al., 2000; Greenberg, 1998). Without being a definitive evidence for the presence polymers in comets, the presence of POM-like polymers in the solid state on cometary grains is to date the best interpretation of

observations that have remained puzzling for a long time.

Laboratory work is in progress to understand if the CO and CN extended sources observed in several comets are also originating from the degradation of a complex organic material on cometary grains. This could give us a chance to learn more about this "hidden" organic component of comets before an in-situ investigation.



**Figure 5**: Formaldehyde density profile in comet Halley: measured by Giotto (squares), and calculated with an extended source from polyoxymethylene (continuous line)

### Conclusion

Comets are probably among the most complex bodies of our Solar System. Laboratory simulations and observations (including extended sources) show that their organic composition goes much further than the list of simple volatile compounds detected in their atmosphere. Future space missions are greatly expected as they will tell us about the origin of the solar system and the origin of life on Earth.

**Acknowledgements**: H.C. thanks CNRS for funding in the frame of the French-Egyptian collaboration program.

- Allamandola, L. J., Sandford, S. A., and Valero, G. J. (1988). Photochemical and thermal evolution of interstellar/precometary ice analogs. *Icarus* 76, 225-252.
- Barbier, B., Henin, O., Boillot, F., Chabin, A., Chaput, D., and Brack, A. (2002). Exposure of amino acids and derivatives in the Earth orbit. *Planetary and Space Science* **50**, 353-359.
- Bernstein, M. P., Allamandola, L. J., and Sandford, S. A. (1997). Complex organics in laboratory simulations of interstellar/cometary ices. Advances in space research 19(7), 991-998.

- Bernstein, M. P., Dworkin, J. P., Sandford, S. A., Cooper, G. W., and Allamandola, L. J. (2002). Racemic amino acids from the ultraviolet photolysis of interstellar ice analogues. *Nature* **416**, 401-403.
- Bernstein, M. P., Sandford, S. A., Allamandola, L. J., Chang, S., and Scharberg, M. A. (1995). Organic Compounds Produced By Photolysis of Realistic Interstellar and Cometary Ice Analogs Containing Methanol. *The Astrophysical Journal* **454**, 327-344.
- Blank, J. G., Miller, G. H., Ahrens, M. J., and Winans, R. E. (2001). Experimental Shock Chemistry of Aqueous Amino Acid Solutions and the Cometary Delivery of Prebiotic Compounds. *Origins of Life and Evolution of the Biosphere* **31**, 15-51.
- Bockelée-Morvan, D., Li, D. C., Wink, J. E., Despois, D., Crovisier, J., Bachiller, R., Benford, D. J., Biver, N., Colom, P., Davies, J. K., Gérard, E., Germain, B., Houde, M., Mehringer, D., Moreno, R., Paubert, G., Phillips, T. G., and Rauer, H. (2000). New molecules found in comet C/1995 O1 (Hale-Bopp). Investigating the link between cometary and interstellar material. Astronomy and Astrophysics 353, 1101-1114.
- Boillot, F., Chabin, A., Buré, C., Venet, M., Belsky,
  A., Bertrand-Urbaniak, M., Delmas, A.,
  Brack, A., and Barbier, B. (2002). The
  Perseus Exobiology Mission on MIR:
  Behaviour of Amino Acids and Peptides in
  Earth Orbit. Origins of Life and Evolution of the Biosphere 32, 359-385.
- Briggs, R., Ertem, G., Ferris, J. P., Greenberg, J. M., McCain, P. J., Mendoza-Gomez, C. X., and Schutte, W. (1992). Comet Halley as an aggregate of interstellar dust and further evidence for the photochemical formation of organics in the interstellar medium. Origins of life and evolution of the biosphere 22, 287-307.
- Chyba, C. F., Thomas, P. J., Brookshaw, L., and Sagan, C. (1990). Cometary delivery of organic molecules to the early earth. *Science* **249**(July), 249-373.
- Cottin, H., Bénilan, Y., Gazeau, M.-C., and Raulin, F. (2004). Origin of cometary extended sources from degradation of refractory organics on grains: polyoxymethylene as formaldehyde parent molecule. *Icarus* 167, 397–416.
- Cottin, H., Gazeau, M. C., Bénilan, Y., and Raulin, F. (2001). Polyoxymethylene as parent molecule for the formaldehyde extended source in comet Halley. *The Astrophysical Journal* 556(1), 417-420.

- Cottin, H., Szopa, C., and Moore, M. H. (2001). Production of hexamethylenetetramine in photolyzed and irradiated interstellar cometary ice analogs. *The Astrophysical Journal Letters* **561**(1), L139-L142.
- Crovisier, J. (1997). Formation and evolution of solids in space, Erice.
- Despois, D., Crovisier, J., Bockelée-Morvan, D., Biver, N.(2002), Comets and prebiotic chemistry: the volatile component, ESA SP-518: Exo-Astrobiology, 123.
- Gerakines, P. A., and Moore, M. H. (2001). Carbon suboxide in astrophysical ice analogs. *Icarus* **154**(2), 372-380.
- Gerakines, P. A., Moore, M. H., and Hudson, R. L. (2000). Carbonic acid production in H\_2O:CO\_2 ices. UV photolysis vs. proton bombardment. *Astronomy and Astrophysics* **357**, 793-800.
- Greenberg, J. M. (1998). Making a Comet Nucleus. Astronomy and Astrophysics **330**, 375-380.
- Greenberg, J. M., and Li, A. (1997). Silicate coreorganic refractory mantle particles as interstellar dust and as aggregated in comets and stellar disks. *Advances in Space Research* **19**(7), 981-990.
- Greenberg, J. M., and Li, A. (1998). From interstellar dust to comets : the extended CO source in comet Halley. *Astronomy and Astrophysics* **332**, 374-384.
- Greenberg, J. M., Li, A., C. X. Mendoza-Gómez, Schutte, W. A., Gerakines, P. A., and Groot, M. d. (1995). Approaching the Interstellar Grain Organic Refractory Component. *The Astrophysical Journal* 455, L177-L180.
- Greenberg, J. M., and Mendoza-Gomez, C. X. (1993). Interstellar dust evolution : a reservoir of prebiotic molecules. *In* "The chemistry of life's origins" (Greenberg, Ed.), pp. 1-32. Kluwer Academic, Netherland.
- Hudson, R. L., and Moore, M. H. (2002). The N3 Radical as a Discriminator between Ionirradiated And UV-photolyzed Astronomical Ices. *The Astrophysical Journal* 568, 1095-1099.
- Jenniskens, P., Baratta, G. A., Kouchi, A., Groot, M. S. D., Greenberg, J. M., and Strazzulla, G. (1993). Carbon dust formation on interstellar grains. Astronomy and Astrophysic 273, 583-600.
- Kasamatsu, T., Kaneko, T., Saito, T., and Kobayashi, K. (1997). Formation of organic compounds in simulated interstellar media with high energy particles. *Bulletin of the Chemical Society of Japan* **70**, 1021-1026.
- Kissel, J., and Krueger, F. R. (1987). The organic component in dust from comet Halley as

mesured by the PUMA mass spectrometer on board Vega 1. *Nature* **326**(April), 755-760.

- Kobayashi, K., Kasamatsu, T., Kaneko, T., Koike, J., Oshima, T., Saito, T., Yamamoto, T., and Yanagawa, H. (1995). Formation of amino acid precursors in cometary ice environments by cosmic radiation. Advances in Space Research 16(2), (2)21-(2)26.
- Meier, R., Eberhardt, P., Krankowsky, D., and Hodges, R. R. (1993). The extended formaldehyde source in comet P/Halley. *Astronomy and Astrophysics* **277**, 677-691.
- Muñoz Caro, G. M. (2003). PhD Thesis. Leiden Observatory, Leiden.
- Muñoz Caro, G. M., Meierhenrich, U. J., Schutte, W. A., Barbier, B., Arcones Segovia, A., Rosenbauer, H., Thiemann, W. H.-P., Brack, A., and Greenberg, J. M. (2002). Amino acids from ultraviolet irradiation of interstellar ice analogues. *Nature* **416**, 403-406.
- Notesco, G., and Bar-Nun, A. (1996). Enrichment of CO over N2 by their Trapping in Amorphous Ice and Implications to Comet P/Halley. *Icarus* **122**, 118-121.
- Notesco, G., and Bar-Nun, A. (1997). Trapping of Methanol, Hydrogen Cyanide, and n-Hexane in Water Ice, above Its Transformation Temperature to the Crystalline Form. *Icarus* **126**(2), 336-341.
- Notesco, G., Laufer, D., and Bar-Nun, A. (1997). The Source of the High C2H6/CH4 Ratio in Comet Hyakutake. *Icarus* **125**, 471-473.
- Oro, J., and Cosmovici, C. B. (1997). Comets and Life on the primitive Earth. *In* "Astronomical and Biochemical Origins and the Search for Life in the Universe" (C. B. Cosmovici, S. Bowyer, and D. Werthimer, Eds.), pp. 97-120.
- Pendleton, Y. J., Sandford, S. A., Allamandola, L. J., Tielens, A. G. G., and Sellgren, K. (1994). Near-Infrared Absorption spectroscopy of interstellar hydrocarbon grains. Astrophys. J. 437, 683-696.

- Radicati-Di-Brozolo, F., Bunch, T. E., and Chang, S. (1986). Laser microprobe study of carbon in interplanetary dust particles. *Origins of Life and Evolution of the Biosphere* 16, 236-237.
- Schutte, W. A., Allamandola, L. J., and Sandford, S. A. (1993a). An Experimental Study of the Organic Molecules Produced in Cometary and Interstellar Ice Analogs by Thermal Formaldehyde Reactions. *Icarus* 104, 118-137.
- Schutte, W. A., Allamandola, L. J., and Sandford, S. A. (1993b). Formaldehyde and organic molecule production in astrophysical ices at cryogenic temperatures. *Science* 259(19 February), 1143-1145.
- Strazzulla, G. (1997). Ion irradiation : its relevance to the evolution of complex organics in the outer solar system. *Advances in Space Research* **19**(7), 1077-1084.
- Strazzulla, G., and Baratta, G. A. (1991). Laboratory study of the IR spectrum of ion-irradiated frozen benzene. Astronomy and Astrophysic 241(1), 310-316.
- Strazzulla, G., Baratta, G. A., Johnson, R. E., and Donn, B. (1991). Primordial comet mantle : irradiation production of a stable, organic crust. *Icarus* 91, 101-104.
- Szopa, C., Sternberg, R., Raulin, F., and Rosenbauer, H. (2003). What can we expect from the in situ chemical investigation of a cometary nucleus by gas chromatography: First results from laboratory studies. *Planetary and Space Science* 51, 863-877.
- Wakamutsu, H., Yamada, Y., Saito, T., Kumashiro, I., and Takenishi, T. (1966). Synthesis of Adenine by Oligomerization of Hydrogen Cyanide. *Journal of Organic Chemistry* 31, 2035-2036.
- Walker, J. F. (1964). "Formaldehyde." American Chemical Society Monograph Series Reinhold, New York.
- Wolman, Y., Miller, S. L., Ibanez, J., and Oro, J. (1971). Science **174**, 1039.