

# Comets and Astrobiology

Hervé Cottin\* and Didier Despois

## Introduction

For a very long time, comets were regarded as bad omens, linked to superstitions, wars, deaths, diseases, etc... But nothing was really known about these wandering objects, suddenly appearing and disappearing in the sky, without prior notice. They were considered by Aristotle as an atmospheric phenomenon and not until the 17th century were they actually seen as astrophysical bodies by western scientists.

In a milestone paper, F. Whipple describes in 1950 comets as “dirty snowballs”, a mixture of ices (dominated by water) and minerals.<sup>7</sup> This model has long since evolved: more is known about the nature of the nucleus from data collected with Earth-based observations, in situ investigations, sample returns and laboratory work. To date, our current knowledge gives comets a privileged location in astrobiology: they are at the crossroads of the origins. Origin of the Solar System, since they have sampled the matter of the Solar Nebula at the place of their accretion, but also, possibly, the origin of life on Earth since comets are rich in water and carbon, two essential constituents of terrestrial life. Therefore part of Earth’s water and carbon might be of cometary origin.

Early last century, Chamberlin and Chamberlin proposed that infalling carbonaceous chondrite meteorites could have been an important source of terrestrial organic compounds.<sup>8</sup> J. Orò was the first in 1961 to suggest that comets may have played a similar role, from observations of carbon- and nitrogen-containing radicals in cometary comae:<sup>9</sup>

*“I suggest that one of the important consequences of the interactions of comets with the Earth would be the accumulation on our planet of relatively large amounts of carbon compounds which are known to be transformed spontaneously into amino acids, purines and other biochemical compounds”.*

An extended coverage of current knowledge about comets is given in the recent book *Comets II*,<sup>10</sup> to which readers that would like to find further information about comets are strongly encouraged to refer to. In the present chapter, Comets will mainly be considered as potential reservoirs of organic molecules for the early Earth. We first present their general characteristics, then the chemical composition of cometary matter as deduced from observations, in-situ exploration, sample returns and laboratory experiments. Anticipated results from the Rosetta mission are then presented and more specifically the instruments designed to probe the molecular composition of the cometary environment: COSAC, COSIMA, MIRO and VIRTIS. Finally, the various potential cometary contributions to the early Earth are addressed.

## Comets in the Solar System

Comets are leftovers of the formation of planets in the Solar System. They formed in the first Myrs in the colder part of the protosolar nebula, where the temperature was low enough for water ice to condense, embedding “dust” particles made of organic and/or mineral material. The resulting “dirty snowball” is the nucleus of the comet, with typical sizes of 1 to 100 km: the nucleus of the famous comet 1P/Halley has an irregular shape, roughly  $8 \times 8 \times 16$  km. It was measured from pictures taken during flyby of the ESA probe Giotto in 1986.

Most comets reside in two reservoirs: i) a large ( $10^5$  AU<sup>3</sup>) and spherical reservoir, the Oort cloud, with an estimated number of comets about  $10^{11}$  to  $10^{12}$ , for a total mass of 1 to a few tens Earth mass and ii) a rather flat disk beyond Neptune orbit, the Kuiper Belt, smaller than the Oort Cloud (100 to 1000 AU at most) and containing also many 1000-km class objects (dwarf planets) like Pluto and the recently discovered Eris, Sedna and Quaoar trans-Neptunian objects (TNO). Part of the Kuiper belt objects were formed at the same distance from the Sun as they are located now, but another part of the Kuiper belt objects and the whole Oort cloud objects were formed closer to the Sun and later moved to their present location due to gravitational interaction with the giant planets Jupiter, Saturn, Uranus and Neptune.

Most of our information about the nucleus composition is indirect and comes from ground based or in situ observation of the gas and particles which are released by the nucleus when it comes close to the Sun. The typical comet loss of material for one return would represent a decrease by about 1 meter of its radius, if averaged over the whole surface.

Gas and dust particles expand in a more or less spherical shell, the coma, which may reach 1 million km for some species quite resistant to photodissociation and photoionisation by solar radiation. Comet tails result from the interaction of coma ions with the solar wind and of coma dust particles with the solar radiation pressure (a neutral sodium tail has also been observed). Tails can extend up to 100 million km, almost the Earth-Sun distance. Although much more visible than the nucleus, the coma and the tails have extremely low densities (below  $10^4$  atoms.cm<sup>-3</sup> in most places (Figs. 5.1-5.2).

<sup>1</sup>1 AU is the average Earth-Sun distance, nearly 150 million km (1 AU =  $1.49610^8$  km)

\*Corresponding Author: Hervé Cottin—LISA, Universités Paris 12 et Paris 7, CNRS, 61 Av. du Général de Gaulle, 94010, Créteil, France.  
Email: cottin@lisa.univ-paris12.fr

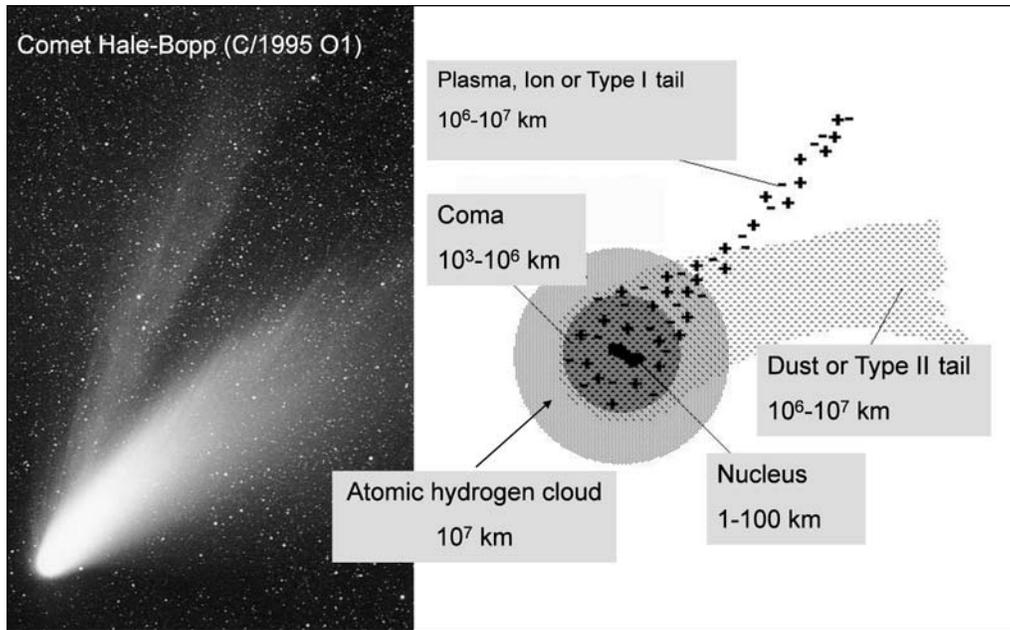


Figure 5.1. Structure of an active comet. The Sun is approximately in the direction opposite to the ion tail.

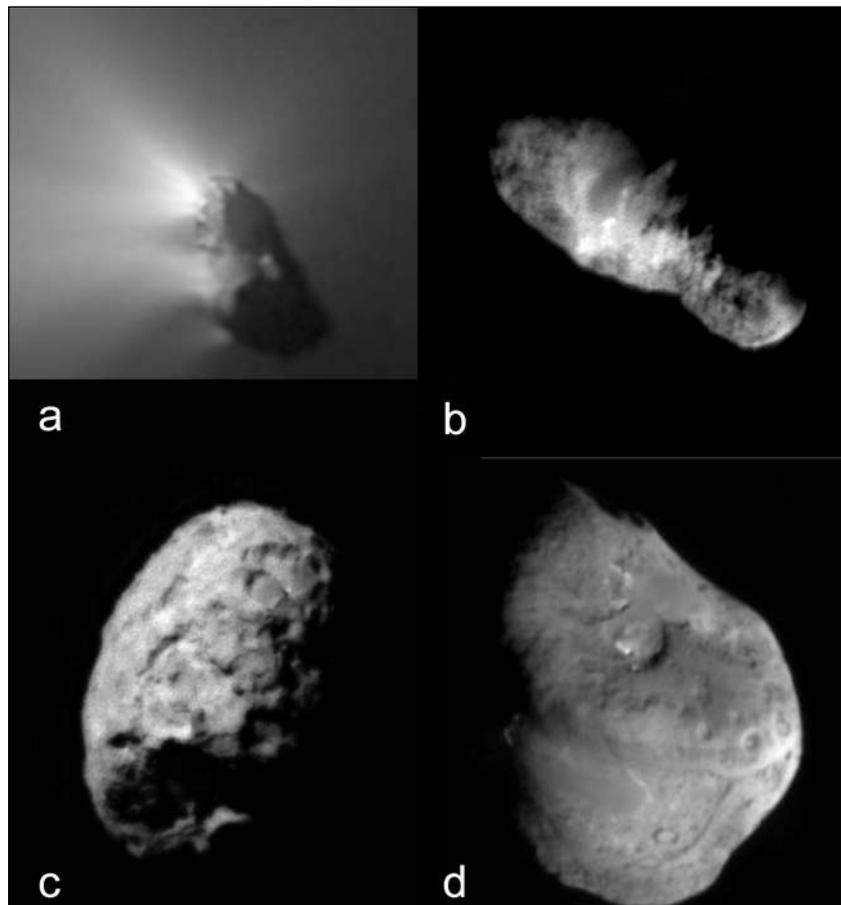


Figure 5.2. Picture of the four nuclei of comets ever observed (as of 2007). a) The nucleus of comet Halley, as seen by the ESA probe Giotto in 1986 from a few thousand km (© ESA and MPAe). b) The nucleus of comet P/Borrelly observed by NASA probe Deep Space 1 in 2001 from 3400 km (© NASA). c) The nucleus of comet P/Wild 2 observed from 236 km by Stardust, the NASA probe which has returned dust samples collected during the flyby (© NASA). d) The nucleus of comet P/Temple 1 observed by NASA probe Deep Impact from 3000 km (© NASA).

## Chemical Composition of Comets

### Remote Sensing

Radio and Infrared spectroscopy of the coma with large telescopes has led to the confirmation of H<sub>2</sub>O as the major cometary ice, but also to the detection of about thirty other less abundant molecular species: the very abundant CO (1–30% with respect to water) and CO<sub>2</sub> (5%) and also many species of interest for prebiotic chemistry—HCN, NH<sub>3</sub>, H<sub>2</sub>CO, H<sub>2</sub>S (at the percent level), HC<sub>3</sub>N, CH<sub>3</sub>CN, NH<sub>2</sub>CHO, CH<sub>3</sub>CHO, H<sub>2</sub>CS... (between 0.01 and 1%). Some of these species have important implications in aqueous solution: HCN is the key molecule for the synthesis of adenine and other nucleic bases, H<sub>2</sub>CO for sugars (formose reaction), NH<sub>3</sub>, HCN, H<sub>2</sub>CO and other aldehydes allow Strecker synthesis (and with CO<sub>2</sub> Bucherer-Berg synthesis) of amino acids and related species. Table 5.1 lists the typical relative abundances of volatile molecules in comets as deduced from coma observations, together with the observed comet-to-comet variation.<sup>11</sup>

Concerning the mineral component of comets, infrared remote spectroscopy with the ISO satellite showed the presence of forsterite, a magnesium rich crystalline silicate.<sup>12</sup> Both amorphous and crystalline silicates are shown to be present. A recent reanalysis of these data<sup>13</sup> provided a tentative detection of carbonates, whereas the detection or not of polycyclic aromatic carbons (PAHs) from the same data remains controversial.

Recently, Deep Impact mission has provided a new original set of data about comets. On July 4th, 2005, a 370 kg impactor collided with comets 9P/Tempel 1 with a relative rate of about 10 km/s. Both impactor and impactor-carrier spacecraft took pictures of the cometary nucleus, while most of the science measurements were performed from Earth telescopes. The impact was a success and resulted in a large amount of new information about the nucleus properties, but no new organic volatile compound was detected. The cometary activity of the comet during the impact looked in many ways like a natural outburst of the comet.<sup>14</sup>

### In Situ Measurements

In 1986 mass spectrometers onboard the Giotto and Vega spacecrafts provided in situ information about dust particles composition during their Halley flyby. They analyzed organic refractory particles, later named CHON particles (from C, H, O, N atoms) and silicate grains. Mass spectrometry showed the presence of large molecular weight molecules, including possibly polymers of H<sub>2</sub>CO.<sup>15</sup> A large amount of such heavy species was detected, but due to the rather low resolution of the mass spectra many different species are mixed in the same measurement channels. In most cases individual identification was not possible.<sup>16,17</sup>

Dust and ice abundances in a comet are of the same order, within a factor of 10—the comet to comet variation may reflect initial composition differences and/or comet evolution due to several orbits in the inner Solar System. Within the dust particle population, silicates and organic refractory material have comparable masses.

### Sample Return Mission

The Stardust mission (NASA) was the very first spacecraft aimed to collect samples from a comet (81P/Wild 2) and return it to Earth.<sup>18</sup> This comet is relatively new in the inner Solar System, as it passed only a few times in the Sun vicinity. Dust grains have been trapped during the comet flyby in a very low density silicon-based aerogel (porosity >99%), designed to allow a progressive deceleration of the captured material, in order to minimize any alteration by heating and pyrolysis of organic molecules. Once brought back to Earth, physical properties and chemical composition of part of the grains have been analysed with the most recent and sensitive instru-

ments. Some of the material is kept untouched for future analyses by new methods to be developed in years to come.

More than 10,000 particles (from 1 to 300 μm) were captured in the coma of comet 81P/Wild 2 and returned to Earth, for a total mass of about 3 × 10<sup>-4</sup>g.<sup>19</sup> First analyses show an extreme complexity of the cometary material.

The Stardust samples contain amorphous and crystalline silicates such as olivine and pyroxene. The presence of crystalline minerals is an indication that some of the material has been processed at very high temperature (more than 1000 K), while part of the silicate is still in an amorphous form, an indication of a completely different thermal history. Those results suggest that the cometary material is a mixture of matter from different origins in a relatively well mixed Solar Nebula.

From an organic chemistry point of view, the first analyses of grains have enabled the detection of an organic component, which is rich in oxygen and nitrogen compared to the one found in carbonaceous meteorites. The samples are very heterogeneous and show N/C ratios ranging from 5 × 10<sup>-3</sup> to 1. Aromatic molecules have been observed, such as naphthalene (C<sub>10</sub>H<sub>8</sub>), phenanthrene (C<sub>14</sub>H<sub>10</sub>) and pyrene (C<sub>16</sub>H<sub>10</sub>), but the samples tend to be poorer in aromatics than are meteorites and interplanetary dust particles. CH<sub>2</sub>, CH<sub>3</sub>, aromatic CH, OH and C = O groups have been identified by infrared spectroscopy. Detection of carboxyl, nitrile and amide functions are also reported after XANES (X-ray absorption near-edge spectroscopy) analyses.<sup>20,21</sup> More specific detection of methylamine (CH<sub>3</sub>-NH<sub>2</sub>), ethylamine (CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub>) and glycine (NH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H) have also been reported, but are still very tentative until further specific isotopic measurements are conducted. Several years of extremely careful work are still ahead before it is possible to reach final conclusions from Stardust sample.

### Laboratory Work

For a better insight into the most complex and less volatile material, one can also 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 (Fig. 5.3). Mayo Greenberg, who conceived that kind of experiments, called this residue “Yellow Stuff”.<sup>22</sup>

The diversity of organic compounds synthesized during such laboratory simulations is remarkable but their identification is seldom exhaustive.<sup>23</sup> The nature of the complex molecules depends on the ice composition and the nature of the energy source. The three kinds of energetic processing used during the experiment (thermal cycle, UV photolysis, energetic particles irradiations) can occur to ice mixtures either on icy coated dust grains in interstellar clouds (potentially precometary ices), or within the Solar Nebula during the accretion of icy planetesimals, or in the outer layers of comet ices in the Solar system. 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 still in progress to address this question.

From an astrobiological point of view, it must be noted that a great number of amino acids (such as glycine, alanine, sarcosine, valine, proline, serine etc...) are reported 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

Table 5.1 Molecules detected in comets and some upper limits

Cometary Volatiles Category	Molecule	Hale-Bopp Abundance (H <sub>2</sub> O = 100)	Intercomet Variation	Detected Comets + Upperlimits	
H	H <sub>2</sub> O	100			Water
	H <sub>2</sub> O <sub>2</sub>	<0.03			Hydrogen peroxide
C,O	CO	23	<1.4-23	9 + 8	Carbon monoxide
	CO <sub>2</sub>	6	2.5-12	4	Carbon dioxide
C,H	CH <sub>4</sub>	1.5	0.14-1.4	8	Methane
	C <sub>2</sub> H <sub>6</sub>	0.6	0.1-0.7	8	Ethane
	C <sub>2</sub> H <sub>2</sub>	0.2	<0.1-0.5	5	Acetylene
	C <sub>4</sub> H <sub>2</sub>	0.05?			Butadiyne
C,O,H	CH <sub>3</sub> C <sub>2</sub> H	<0.045			Propyne
	CH <sub>3</sub> OH	2.4	<0.9-6.2	25 + 2	Methanol
	H <sub>2</sub> CO	1.1	0.13-1.3	18 + 3	Formaldehyde
	CH <sub>2</sub> OHCH <sub>2</sub> OH	0.25			Ethylene glycol
	HCOOH	0.09	<0.05-0.09	3 + 2	Formic acid
	HCOOCH <sub>3</sub>	0.08			Methyl formate
C,O,H upper limits	CH <sub>3</sub> CHO	0.025			Acetaldehyde
	H <sub>2</sub> CCO	<0.032			Ketene
	c-C <sub>2</sub> H <sub>4</sub> O	<0.20			Oxirane
	C <sub>2</sub> H <sub>5</sub> OH	<0.1			Ethanol
	CH <sub>2</sub> OHCHO	<0.04			Glycolaldehyde
	CH <sub>3</sub> OCH <sub>3</sub>	<0.45			Dimethyl ether
	CH <sub>3</sub> COOH	<0.06			Acetic acid
N	NH <sub>3</sub>	0.7	<0.2-1	4	Ammonia
	HCN	0.25	0.08-0.25	32 + 0	Hydrogen cyanide
	HNCO	0.1	0.02-0.1	4 + 2	Isocyanic acid
	HNC	0.04	<0.003-0.035	12 + 3	Hydrogen isocyanide
	CH <sub>3</sub> CN	0.02	0.013-0.035	9 + 2	Methyl cyanide
	HC <sub>3</sub> N	0.02	<0.003-0.03	3 + 7	Cyanoacetylene
	NH <sub>2</sub> CHO	0.015			Formamide
	NH <sub>2</sub> OH	<0.25			Hydroxylamine
N upper limits	HCNO	<0.0016			Fulminic acid
	CH <sub>2</sub> NH	<0.032			Methanimine
	NH <sub>2</sub> CN	<0.004			Cyanamide
	N <sub>2</sub> O	<0.23			Nitrous oxide
	NH <sub>2</sub> -CH <sub>2</sub> -COOH	<0.15			Glycine
	C <sub>2</sub> H <sub>5</sub> CN	<0.01			Cyanoethane
	HC <sub>5</sub> N	<0.003			Cyanobutadiyne
	S	H <sub>2</sub> S	1.5	0.13-1.5	15 + 5
OCS		0.4	<0.09-0.4	2 + 5	Carbonyl sulfid
SO		0.3	<0.05-0.3	4 + 1	Sulfur monoxide
SO <sub>2</sub>		0.2			Sulfur dioxide
CS <sub>2</sub>		0.17	0.05-0.17	15 + 3	Carbon disulfid
H <sub>2</sub> CS		0.02			Thioformaldehyde
S <sub>2</sub>		0.005	0.001-0.005	5	Disulfur
CH <sub>3</sub> SH		<0.05			Methanethiol
NS		0.02	<0.02-0.02	1 + 1	Nitrogen sulfide
P		PH <sub>3</sub>	<0.16		
	Metals				
Metals	NaOH	<0.0003			Sodium hydroxide
	NaCl	<0.0008			Sodium chloride

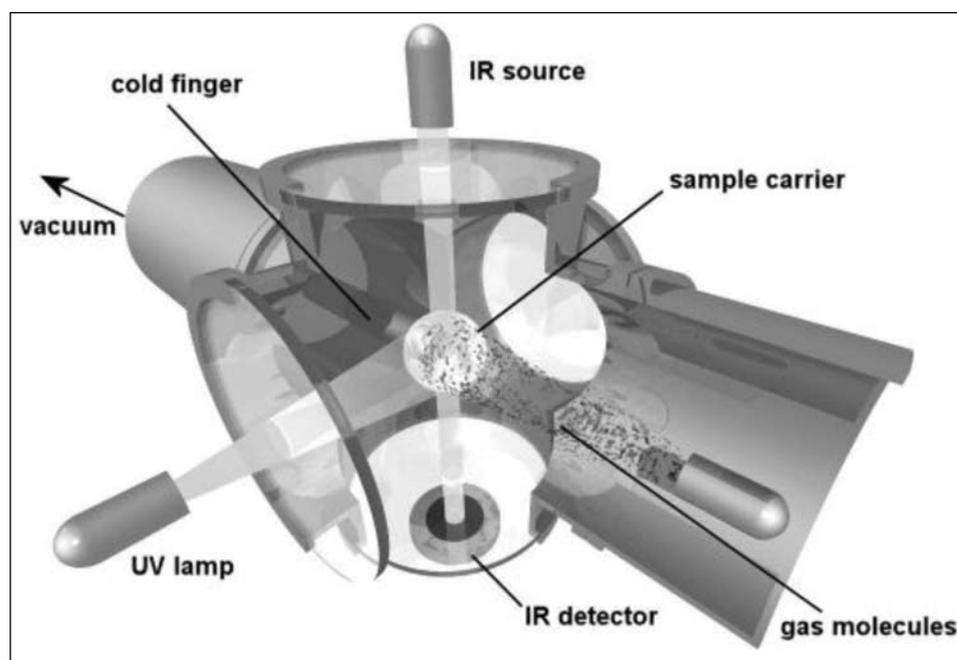


Figure 5.3. A typical experimental setup allowing the photolysis of cometary ice analogs made by deposition of a gas mixture on a cold sample carrier cooled down to 10 K in a cryostat (the UV lamp can be replaced in some setups by an ion or an electron gun). The ice evolution can be analysed in situ by infrared spectroscopy. 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 others. Picture courtesy of Jan Hendrik Bredehoft, University of Bremen, thoralf@uni-bremen.de.

H<sub>2</sub>O: CH<sub>3</sub>OH: NH<sub>3</sub>: CO: CO<sub>2</sub>. Unhydrolyzed residues (without any liquid water introduced to the analysis protocol) produce only a trace of glycine. The detection of the other amino acids requires an acid hydrolysis of the residue under very strong conditions (HCl ≥ 6 M and T ≥ 100 °C).<sup>24,25</sup> 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.

The chirality issue has also been investigated through laboratory simulations. It has been reported that an asymmetric vacuum UV photolysis of a racemic mixture of leucine in the solid state results in the production of an enantiomeric excess of one form of the amino acid.<sup>26</sup> However, such an enantiomeric excess has not been detected yet when amino acids are directly synthesised within an ice mixture under circularly polarized light.<sup>27</sup> Further work on this topic is planned with the opening of the new French synchrotron SOLEIL in 2007 (beamline DESIRS).

Following remote sensing and in situ observations which can only probe the atmosphere of comets, sample return of a limited amount of cometary material and laboratory work on simulated cometary ices, an ambitious next step is the landing on a comet to study its composition. This will be achieved with the Rosetta mission from the European Space Agency (ESA).

### Rosetta 2014—Rendezvous of a Laboratory with a Comet

The Rosetta mission is made of two parts: one orbiter revolving around the nucleus and a lander called Philae. It was launched on March 2<sup>nd</sup> 2004 and will reach its target, comet 67P/Churyumov-Gerasimenko in August 2014. The landing of Philae on the nucleus of the comet is expected in November 2014. The instruments onboard the orbiter will enable an unprecedented

analysis of the composition of volatile and refractory compounds released from the nucleus. Two mass spectrometers on board Rosetta (ROSINA: Rosetta Orbiter Spectrometer for Ion and Neutral Analysis, COSIMA: COmetary Secondary Ion MASS spectrometer) will collect and analyse gas and dust as close as 1 km from the surface of the nucleus, hopefully close enough to study almost unaltered matter released from the nucleus. Four spectrometers will also probe the composition of the cometary environment on a broad spectral range of electromagnetic radiation (OSIRIS: Optical, Spectroscopic and Infrared Remote Imaging System, ALICE: UV spectrometer, VIRTIS: Visible and InfraRed Thermal Imaging Spectrometer, MIRO: Microwave Instrument for the Rosetta Orbiter). On board Philae, the most fruitful information from an astrobiological point of view will come from COSAC (Cometary Sampling and Composition experiment), a gas chromatograph coupled with a mass spectrometer. In this chapter, we emphasize some of these instruments (COSAC, COSIMA, VIRTIS and MIRO) because most of the new organic molecules should be detected thanks to these experiments.

#### COSAC

The COSAC instrument is a gas chromatograph (GC) coupled with a mass spectrometer (MS, a linear time of flight spectrometer in this case). It consists of 8 chromatographic columns; each of them is connected to its own detector (TCD), but it is also possible to connect them to a mass spectrometer.<sup>28</sup> Previous results obtained thanks to direct mass spectrometry measurements with Puma, Giotto and Stardust spacecrafts gave “only” the mass spectrum of the mixture of all the molecules at the same time. COSAC will carry out a preliminary separation by chromatography, which will achieve a quasi definite identification of the compounds since they will be recognised both from their retention time and from their individual mass spectra. Samples will be collected after drilling the surface and heated at various temperatures before being injected into the analysis system. Pyrolysis (up to 600 °C) is possible in order to degrade the

most refractory components and enable gas phase analysis of the fragments. Out of the eight chromatographic columns, three are specifically devoted to the analysis of chiral molecules in order to distinguish enantiomers. The other five columns have been selected so that a maximum of molecules can be detected. Moreover, the simultaneous analysis of a single sample with several columns (up to four columns at the same time) will facilitate data analysis by comparison and thus increase the reliability of interpretation.

Many molecules were considered in the selection of the chromatographic columns (molecules already detected in the atmosphere of comets, in the interstellar medium, or from laboratory simulations of cometary ices). One must note that amino acids and other heavy compounds such as oxalic acid, urea, etc... are not detectable, since they are not volatile enough to be analysed in the gaseous phase. GC analysis of such compounds requires a preliminary stage of processing called derivatization (chemical reaction making the targeted compound more volatile). This procedure is not feasible with the COSAC instrument, but work is in progress to include derivatization in future Martian exploration experiments. Nucleus analyses by the COSAC instrument will be completed by CIVA (infrared analysis) and MODULUS (for isotopic measurements).

### COSIMA

COSIMA is a time-of-flight secondary ion mass spectrometer (TOF-SIMS) instrument dedicated to in situ analysis of cometary dust grains.<sup>29</sup> Cometary grains will be collected on metallic targets (silver, gold, palladium and platinum) and an optical system (COSISCOPE) will locate cometary grains for further analysis with TOF-SIMS. COSIMA has a mass resolving power ( $M/\Delta M$ ) of about 2000 and will be able to analyse particles with a resolution around 50  $\mu\text{m}$ . The TOF-SIMS technique is very sensitive to the composition of the surface and it only analyzes the very first mono-layers of the sample. TOF-SIMS spectra are difficult to interpret as they contain a very large amount of information, showing both elemental and molecular masses up to masses  $\sim 1000$  amu.

Unlike analyses performed with COSAC, no separation of the different molecules is performed prior to analysis by mass spectroscopy. Therefore extremely complex spectra are expected. Quite a secure distinction between the organic and mineral components can easily be achieved (molecules rich in H such as organic compounds tend to have a mass a few fractions of decimal above the unit,  $m = n + \delta$  with  $n \in \mathbb{N}$ , while mineral masses tend to be below the unit,  $m = n - \delta$ ). Any specific identification might be hazardous unless careful calibration is performed with a ground instrument, which is currently already in progress. The instrument has a very high resolution in mass and also a spatial resolution which can allow analysis of the composition of several spots on the same grain. Moreover, COSIMA can analyse non volatile compounds, which are not possible to detect with COSAC.

Analyses by the COSIMA instrument will be completed by ROSINA for the gaseous phase.<sup>30</sup> This instrument based on mass spectrometry measurements will determine the composition of the atmosphere and ionosphere of a comet thanks to two sensors. ROSINA has a wide mass range (1 to  $> 300$  amu) and a very high mass resolution  $M/\Delta M > 3000$  with the ability to resolve CO from  $\text{N}_2$  and  $^{13}\text{C}$  from  $^{12}\text{CH}$ .

### VIRTIS and MIRO

The two spectrometers VIRTIS and MIRO will observe the nucleus and the coma from the orbiter. They will provide information on the physical conditions and physical processes in the comet and on its chemical composition.

Virtis is a UV/Visible and infrared spectrometer.<sup>31</sup> Two channels cover respectively the 0.2-1 microns and 1-5 microns wavelength ranges. The infrared channel will provide information on the nature

of the comet surface and on molecules ("parent molecules") released in the coma before they are photodissociated, ionized or react with other species.

On the nucleus, the minerals and ices will be remotely mapped with high spatial resolution. Silicates and hydrates are expected; if present, phyllosilicates ("clay") will show up through their water and OH absorption bands. Water ice itself and other ices like  $\text{NH}_3$ ,  $\text{CO}_2$  or  $\text{H}_2\text{S}$  can be identified by their infrared spectral features. Hydrocarbon ices ( $\text{CH}_4$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ ) can also be identified in this spectral range. Some of these simple hydrocarbons could also have polymerized. Such carbonaceous material will redden the comet spectrum; a more precise identification requires however a high signal to noise ratio ( $> 100$ ).

In the coma, beside solid features coming from the grains, much narrower features coming from the gas phase are present. A major objective is the identification of the hydrocarbon emission in the 3-4 micron range, through the high ( $\lambda/\Delta\lambda > 2000$ ) spectral resolution. The infrared spectrum is also rich in rovibrational emission of important parent molecules:  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{CO}$ ,  $\text{CH}_3\text{OH}$ , CO. Deuterated water HDO can also be detected with long integration times; the HDO/ $\text{H}_2\text{O}$  ratio is a key information for evaluating the importance of comets in the build up of Earth oceans. Current data are only available for 3 comets (Halley, Hyakutake and Hale Bopp) and point to a D/H ratio in water in comets ( $\sim 3 \cdot 10^{-4}$ ) twice that in SMOW (standard mean ocean water  $\sim 1.5 \cdot 10^{-4}$ ). But the few observed comets are not thought to be representative of all comets and the homogeneity of this ratio at different locations in a given comet is also an open question.

The UV channel of Virtis is mainly sensitive to the products of coma processes ("daughter molecules"): radicals (OH, CN,  $\text{C}_2$ ,  $\text{C}_3$ , NH, CH), ions ( $\text{CO}^+$ ,  $\text{CH}^+$ ,  $\text{H}_3\text{O}^+$ ,  $\text{N}_2^+$ ) and small molecules (CO). The nature of the parent can be constrained to some extent; this is especially interesting if one suspects these species to be the photo or thermal degradation products of complex organics expected in cometary grains. The presence of polymers like the  $\text{H}_2\text{CO}$  polymer polyoxymethylene (POM), or HCN polymers can thus be indirectly tested.

The MIRO instrument consists of two radio receivers operating at mm and submm wavelength (1.6 mm and 0.5 mm, or 190 and 562 GHz).<sup>32</sup> Due to the small antenna size (30 cm) and the absence of cryogenic cooling of the receiver, only major cometary species will be observed:  $\text{H}_2\text{O}$  (and its isotopes  $\text{H}_2^{17}\text{O}$  and  $\text{H}_2^{18}\text{O}$ ), CO,  $\text{CH}_3\text{OH}$  and  $\text{NH}_3$ . The precise physical data on the nucleus outgassing and the development of the coma deduced from these observations will be used for detailed modelling of the observations performed with the much larger ground-based instruments like the IRAM 30m in Spain, LMT 50 m in Mexico, GBT 110 m in Virginia or the ALMA interferometer under construction in Chile (64 antennas of 12 m diameter).  $\text{NH}_3$  itself is quite difficult to observe from the ground and has only been detected in very few comets using cm radiowave or near IR. From its Earth orbit, the ODIN satellite provided tentative detections of  $\text{NH}_3$  in two comets using the same 572GHz line as MIRO. The presence of  $\text{NH}_3$  in Solar System icy objects lowers the water ice melting point and thus allows water to be liquid at temperatures lower than for pure water.

## Comets and Life

### Delivery of Prebiotic Molecules

The exogenous source of prebiotic molecules involves impacts by large objects, comets and asteroids on the one hand and soft landing of micron to mm sized interplanetary dust grains of cometary or asteroidal origin on the other hand. The conditions for delivery by these two mechanisms are very different and the yields are very

difficult to assess, but both may be quantitatively important to fueling the stock of prebiotic species.<sup>33</sup> We concentrate here on the cometary part.

### A. Violent Delivery by Impacts

At first thought, impacts of comet nuclei on the Earth seem to be such highly energetic processes that all molecules should be destroyed. It has been shown however through laboratory experiments and numerical simulations that an impact, if in a grazing geometry, could have delivered to early Earth some amino-acids (like aspartic and glutamic acids) in comparable amounts to those produced by Miller-Urey synthesis in a CO<sub>2</sub> rich atmosphere.<sup>34</sup> If one considers smaller bodies like Mars, Europa or the Moon, despite a lower impact velocity favourable to molecule survival, the yield is lower as a large fraction of the impacting material can escape owing to the lower gravity; this results in impacts being still relatively efficient in the case of Mars and much less so for the smaller Europa or the Moon. However, even if Europa's formation history did not allow for the inclusion or in-situ formation of organics, Europa could have gained some organic molecules through such cometary impacts.

One should note that asteroids (some of which being organic-rich) do not have a similar organics delivery efficiency on account of their more rigid, less porous and higher density interior. Higher temperatures would be reached during the impact resulting in a higher rate of destruction of the complex molecules.

### B. Softly Decelerated Stratospheric Interplanetary Dust Particles (SIDPs) and Soft-Landing Micrometeorites

Small (10 microns) particles are efficiently decelerated by the atmosphere and "float around" long enough to allow their collection by airborne collectors. The fluffiest of these so-called Brownlee particles are thought to be of cometary origin. Somewhat larger 100-200 micron particles reach the ground and are called micrometeorites. They can be collected in polar ices, where they are more easily identified and less contaminated by Earth particles. SIDPs and micrometeorites are a regular source of extraterrestrial matter coming to the Earth; estimated at 10,000 to 40,000 tons/year, they are second in importance after the large impacts (when their contribution is averaged over geological times).

A fraction of these particles is carbon rich, even richer than carbonaceous chondrites. In a sample of C rich micrometeorites, two amino acids have been found, AIB and isovaline, the latter being absent in living organisms on Earth.

### C. Atmospheric Shock Synthesis

Besides the organic molecules they carry and may deliver to Earth, infalling bodies input energy into the atmosphere. This leads to shock induced chemical syntheses, which are rather efficient in a reducing, Urey-Miller type atmosphere, but much less so in a weakly reductive atmosphere (where H<sub>2</sub>/CO<sub>2</sub> < 0.1).

### Comets as Life Frustrators?

Comets may represent, depending on the epoch (and on models), 1 to 50% of the km-size bodies impacting the Earth. Whereas such impacts may have been favourable to the appearance of life through the delivery or the shock-induced syntheses of organic molecules, they also may be detrimental and possibly lethal to incipient life. The possible cometary nature of two famous events is still being debated: the 1908 Tunguska event (a few ten meters body), which destroyed 2000 km<sup>2</sup> of Siberian forest and the K/T event 65 Myr ago, which has produced the Chixculub crater (from a >10 km body) and is a favourite explanation for the contemporary mass extinctions (including dinosaurs).<sup>35</sup>

### Liquid Water in Comets?

Could advanced prebiotic chemistry take place in the comets themselves, leading to the possibility for the appearance of life in comets? Such a question makes sense especially if liquid water can exist in comets. Liquid water requires a high enough temperature and pressure. During comet formation, the accretion process heats mainly the surface of the comet. Two other mechanisms can generate heat inside the nucleus: radioactive heating and amorphous to crystalline ice (irreversible) transformation. Al<sup>26</sup> is by far (by a factor of 500) the most important radiogenic heating element at early times in the Solar System. With a lifetime  $\tau_{1/2}$  of 700,000 years, it is widespread in the interstellar medium and thought to have been present in the protosolar nebula. It can heat the interior of comets if they are large enough to avoid rapid cooling by heat conduction or gas diffusion; but this could happen only if these comets have formed very rapidly (< a few  $\tau_{1/2}$ ). According to numerical models, 10 km-size comets could typically harbour liquid water for 10<sup>5</sup> yrs.<sup>36</sup>

### Conclusion

Comets can bring to the Earth elements like carbon, as well as water (in an amount which remains to be determined). Moreover, they contain simple organic molecules and it is probable that they contain more complex ones as well. Thus comets are likely contributors to early Earth enrichment in prebiotic molecules, through the dust particles they release (some of which end up encountering the Earth atmosphere), through atmospheric chemical syntheses and possibly also through direct delivery taking place when cometary nuclei impact the Earth. These same impacts may also strongly affect later developments of life, either locally or on a planetary scale.

Many questions are central to the current debates, which we hope will find a response in the coming years and for which space missions can bring important results:

- Where and when were the cometary matter and then the comets, formed?
- How close is cometary matter to interstellar matter?
- Do comets contain amino acids and other bricks of life?
- Do these molecules present an enantiomeric excess, or are they in racemic mixture?
- What is the precise budget of the cometary contributions to the Earth (fraction of the water of the oceans; fraction of carbon; fraction of prebiotic molecules)?
- What is the global effect of comets on life, its appearance and its development?
- Out of the Solar System, is the presence of an Oort cloud or a Kuiper belt an exceptional characteristic of our Solar System or a banal fact among main sequence stars? Given the crucial part potentially played by comets in the origin and the evolution of life on Earth, it appears fundamental to know the probability for a star with habitable planets to be also surrounded by comets. New research topics thus arise regarding these exocomets (comets orbiting around other stars). The properties of the spectra of a close star,  $\beta$  Pictoris—one of the rare main sequence stars around which a disc has been detected—currently are convincingly interpreted as being due to a constant infall of "evaporating bodies" on this star. Much is then to be expected from ambitious recent space experiments like the Corot mission, whose goal is to detect Earth-size planets around a wide range of other stars and which might make it possible also to detect comets directly.<sup>37</sup>

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