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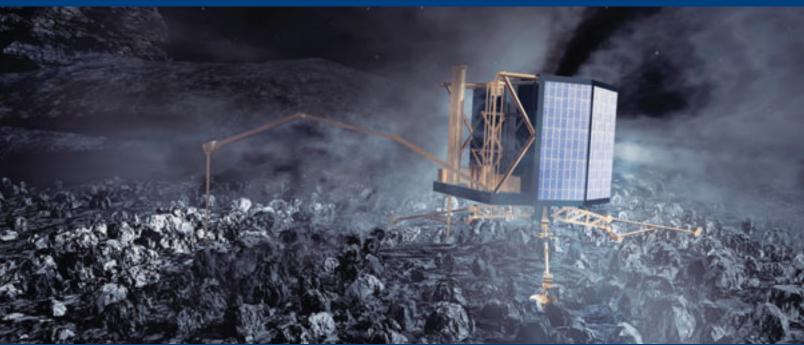
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ANALYZING a COMET NUCLEUS BY Capillary GC



WILL IN SITU STUDIES OF COMETS HELP US DETERMINE WHETHER THE PRECURSORS OF LIFE ON EARTH DRIGINATED IN DUTER SPACE?

ROBERT STERNBERG AND CURIL SZOPA

University of Paris 12 Vale de Marne (France)

CLaude Rodier

University of Poitiers (France)

he search for the origins of life on Earth has captivated humanity since the beginning of time. Our first major breakthrough in understanding our origins was the invention of the astronomical lens by Galileo in 1609. With this first telescope, Galileo confirmed Copernicus's heliocentric model and comprehended the Earth's real place and role in the solar system. Without a doubt, the second major event was the beginning of space exploration, which enabled spacecraft and probes to visit nearly all the planets in Earth's solar system (and most of their satellites) during the past 40 years, thus unveiling the immensity of the universe.

Even if our solar system's formation is now well known and agreed upon—a dense, interstellar, rotating cloud collapsed under its own weight and formed the Sun in its center and the planets orbiting around it in an ecliptic plan—the origin of life is still controversial. Some believe that the starting molecules of the terrestrial prebiotic chemistry nec-

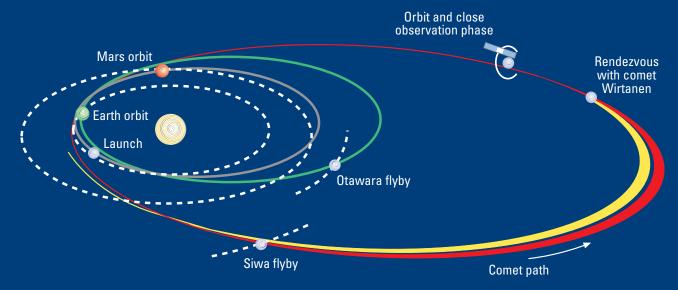


FIGURE 1. Trajectory of Rosetta on its way to the encounter with the comet Wirtanen.

Adapted with permission from an ESA document.

essary for the emergence of life were produced in situ from the chemical evolution of the Earth's primitive atmosphere. Others claim that the oxidative environment of early Earth was unfavorable for such syntheses, and therefore, the key organic molecules must have been imported by the heavy bombardment of meteorites and comets.

Why study comets?

Among the numerous objects of the solar system, comets are of particular interest for the study of our origins. They are small bodies, up to a few kilometers across, made of ice and dust, orbiting the solar system in two reservoirs, the Kuiper belt and the Oort cloud, which are located beyond Neptune at ~30 and 100,000 astronomical units (AU), respectively (1 AU = 150 billion km, roughly equal to the distance between the Earth and Sun), from the Sun on the outer edges of the solar system halfway to the nearest star. They become visible only when a nearby gaseous planet (Jupiter, Saturn, Uranus, or Neptune) or star perturbs their orbits and precipitates them, with an elliptical orbit, into the internal solar system. When a comet approaches the Sun at 1-5 AU, the rising surface temperature of the nucleus sublimates the ices and ejects gas and dust, forming an atmosphere around the nucleus. This atmosphere, called a coma, is visible from Earth.

Comets are assumed to be among the most primitive objects of the solar system, containing traces of its early evolution. Indeed, formed at the same time as the planets (~4.7 Gyr ago) and maintained in the outer solar system where the low temperature and weak radiation would prevent their chemical evolution, comets supposedly have conserved the composition of the solar nebula and, thus, the average composition of the solar system.

Comets also contain high abundances of the extraterrestrial organic material that is supposed to have provided the prebiotic building blocks and water necessary for the emergence and development of life on Earth. It is thus of primary importance to understand the chemical nature of the organic content of the cometary nucleus. To date, there is only indirect information available, mainly from the spectroscopic analysis of cometary

dust and the gas-phase coma; much of the data came from space-craft encounters with comet Halley in 1986. However, these data are quite difficult to interpret because the spectra of all the molecules are superimposed and the instruments used had low resolution. Moreover, the molecules detected have been processed by evaporation from the comet nucleus, irradiation from the sun, and the impact of solar wind particles. To overcome these obstacles and ambiguities, the first direct investigation of a comet nucleus and coma will be carried out by the forthcoming Rosetta cometary space mission, which is scheduled for launch in 2003. Developed by the European Space Agency (ESA), this mission will use a spacecraft with a landing probe designed to carry out a detailed, in situ, molecular and isotopic investigation of a comet nucleus and its close environment.

The primary objective of this article is to show how cometary material can be directly investigated by capillary GC, which is a well-known laboratory analytical technique that has already been used successfully to explore Mars's and Venus's environments. The second objective is to show how the results expected from such an investigation can contribute to a better knowledge of comets' origins and evolution and, therefore, to a better understanding of our own origins. Particular emphasis will be placed on the analytical capabilities of capillary columns used for the GC/MS experiments aboard the Rosetta lander.

How to study comets?

There are three main approaches to study any atmosphere or body in the solar system. The first is direct investigation from ground-based and orbiting observatories using remote sensing techniques (usually spectroscopy) and from in situ measurements performed by on-board atmospheric or landing-probe instruments. The second is laboratory simulation, which attempts to reproduce the evolution of a particular atmospheric composition. In this approach, a representative mixture is subjected to an energy deposition designed to be similar to solar system phenomena, such as photons, cosmic rays, or solar winds. Although all planetary conditions cannot be accurately reproduced, this approach yields precious information on the nature of the molecules that

can be expected; it can also confirm the presence of molecules already detected. The third method is theoretical modeling, which, by using observational and laboratory data—such as reaction pathways and thermodynamic and rate constants—determines the chemical and physical processes that formed the expected, or detected, molecules and their relative abundances.

There appears to be a close interaction between these three methods. Indeed, the characteristic signature of a compound can more easily be identified by direct investigation if predicted data obtained from experimental simulation or modeling are available. Likewise, the definition, implementation, and optimization of an observatory instrument may strongly depend on predicted parameters. This is particularly true for in situ analysis by GC, which requires the selection and calibration of stationary phases in accordance with the nature and chemical family of the expected compounds. In turn, observational data supply the modeling effort with improved and growing data sets, which can validate the models.

The observations of the comae of comets Halley, Hyakutake, and Hale–Bopp through IR and UV spectroscopy were carried out from Earth observatories and several flybys of the Giotto and Vega 1 and 2 probes in 1986 (1, 2), which led to the identification of ~30 organic and inorganic stable molecules, such as HCOOH, H₂CO, and NH₃. Using these observational data, researchers performed laboratory simulation experiments, such as selecting ice mixtures of CO₂, NH₃, and H₂O—which represent the composition of the interstellar medium where cometary ices are supposed to have formed—and irradiating them with high-energy protons. With this approach, researchers synthesized most of the molecules already detected and many others

still not identified by direct investigation. Furthermore, this type of experimental simulation recently created several amino acids, such as glycine and alanine, and aminobutyric acids (after acid hydrolysis), thus strengthening the hypothesis that Earth may have been seeded with amino acids from space in its earliest days.

Theoretical modeling—in particular, of the chemistry developed in the nucleus cannot be very accurate because of the lack of experimental data about the chemical mechanisms and rate constants of reactions involving cometary compounds in the solid state. Nevertheless, some tentatives were proposed to determine the correlations between the molecule and ion products detected in the coma and their likely parent molecules in the nucleus. For example, it has been shown that photodegradation of polyoxymethylene produces gaseous molecules, such as H₂CO, CO, CO₂, HCOOH, and CH₃OH, which are detected in the comae of several comets. Such data, by showing the likely presence of polyoxymethylene in the nucleus, should help researchers interpret and model their observations (3). The first in situ investigation of both the coma and the nucleus of a comet by the Rosetta space mission should provide some of these essential missing data.

GC's heritage in space

Since the beginning of space exploration, most of the probes sent to investigate other planetary atmospheres and surfaces have carried instruments to determine their elemental, isotopic, and molecular (inorganic and organic) compositions. Because MS and GC instruments fulfill the spacecraft's severe constraints on mass, size, mechanical strength, automation, and energy consumption, these techniques remain the most frequently used for in situ chemical analysis. Indeed, they have been successfully used for the exploration of Venus (4) and Mars (5), and they will be used in the atmospheric Huygens probe when the Cassini–Huygens mission (6, 7) launched in October 1997 reaches Titan, Saturn's largest moon (Table 1).

Venus and Mars. Despite its high pressure and temperature, the atmosphere of Venus was explored by several atmospheric probes that included GC instrumentation: the U.S. Pioneer Venus in 1978, the Soviet Venera 11–14 from 1978 to 1982, and Vega in 1985. These chromatographs used packed, parallel columns and thermal conductivity detectors (TCDs) or noble gas ionization detectors with electron-capture detectors. The U.S. Viking mission to Mars landed two giant modules with various instruments to conduct in situ analyses of the Martian atmosphere and soil in 1976. The scientific payload included three experiments specifically devoted to search for microscopic life in the soil.

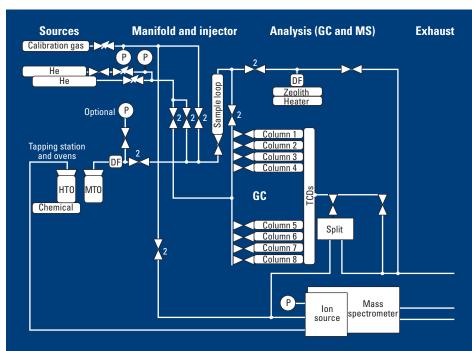


FIGURE 2. Schematic of the COSAC experiment.

DF are dust filters. HTO and MTO are the high- and medium-temperature ovens. P are pressure gauges. Adapted with permission from Ref. 10.

One of these astrobiological sensors, the Gas Exchange Experiment, used a gas chromatograph with one packed column to analyze the gases released by the soil after "digestion" of a nutrient liquid. This experiment did not provide clear and unambiguous results. However, the payload also included a chemical analysis system composed of a pyrolyzer (pyr) device coupled to a GC/MS system, which used a magnetic mass spectrometer and one analytical packed column. This pyr-GC/MS system clearly showed the absence of organic compounds at concentrations higher than the parts-per-million level in the analyzed samples. (However, the samples were collected at depths <10 cm, which is very close to the surface.)

Titan. Titan, the giant satellite of Saturn, is one of the most interesting places in the solar system to study prebiotic chemistry. It has a dense atmosphere composed mainly of N_2 and CH_4 . Traces of other organic compounds were revealed by the Voyager's IR spectrometer in 1980 and 1981 and predicted in laboratory simulations. The atmospheric probe of the Cassini–Huygens mission includes a GC/MS instrument coupled to an aerosol and collector pyrolyzer. It will determine the nature and abundance of organic and inorganic compounds in Titan's atmospheric gas phase and aerosols from an altitude of 170 km to the surface. Three capillary columns operating in parallel will be used to separate the expected species of Titan's atmosphere.

Identification and detection will be achieved by connecting each column to an independent MS ion source. The quadru-

pole mass spectrometer (range = 2-150 amu) will operate in two modes, either coupled to the gas chromatograph or independently, by direct sample injection. For substances such as noble gases and many organic compounds, mixing ratios as low as 0.1 ppb will be detected. The first column is a carbon molecular sieve capillary packed column for the separation of light gases (from N_2 to CH_4). The second one is a wall-coated, opentubular (WCOT) column with a glassy carbon stationary phase for the low-molecular-mass hydrocarbons (C_1-C_3). The third column is a silicosteel WCOT capillary column with a cyanopropylphenyl (CPP) dimethylpolysiloxane stationary phase, which is slightly polar, for the saturated and unsaturated hydrocarbons (C_4-C_8) and the nitriles (up to C_4). It will be the first time that capillary columns have been used in space.

Rosetta and COSAC

The Rosetta mission is a very ambitious exploratory program built by ESA with the aim of landing a probe on a comet and performing in situ analysis of the cometary environment and material collected on and below the surface of the nucleus. This ESA cornerstone mission is scheduled for launch on an Ariane 5 rocket in January 2003. As shown in Figure 1, after an 8-yr cruise phase, including the flybys of two asteroids, the space-craft will intercept the comet and drop a lander on its surface in 2012 (8). The target comet Wirtanen is a short-period, fairly active comet with a radius estimated at 600 m on the basis of

Hubble Space Telescope observations.

The cometary sampling and composition (COSAC) experiment, which involves one of the eight instruments aboard the Rosetta lander, is dedicated to the in situ analysis of the compounds obtained from thermal volatilization of the comet's nucleus material. COSAC, which is depicted in Figure 2, is a pyr-GC/MS system with a total mass of 4.38 kg and was built by Rosenbauer and co-workers (9, 10). The pyrolyzer consists of 16 micro-ovens mounted on a carousel, which can be heated to 800 °C. The GC subsystem includes eight capillary columns mounted in parallel, of which five are devoted to general chemical composition analysis and three to enantiomeric separations. GC detection is performed by a miniaturized TCD connected to each column.

The second part of the analysis is performed by a miniaturized (<1 kg) high-resolution TOF mass spectrometer with a mass range of 12–1500 amu. The instrument has an electron-impact ionization source, a multisphere plate secondary electron amplifier detector, and a time-to-digital converter for signal and flight time registration. The TOF mass spectrometer was developed and tested specifically for the

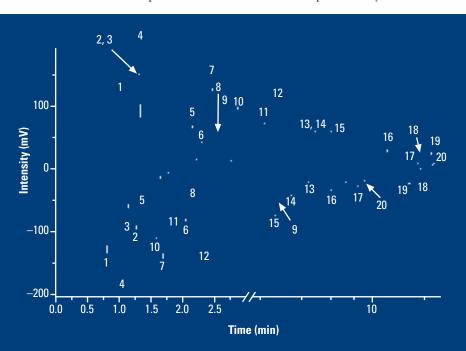


FIGURE 3. Separation of the C_2 – C_6 organic compounds with two columns of the COSAC experiment under space operating conditions (temperature = 30 °C, outlet pressure = 10 mbar).

Peaks: 1, acetaldehyde; 2, pentane; 3, methyl formate; 4, methanol; 5, ethanol; 6, methyl pentane; 7, acetone; 8, hexane; 9, methyl acetate; 10, propan-2-ol; 11, 2 methyl propan-2-ol; 12, acrylonitrile; 13, heptane; 14, methyl propanoate; 15, propionitrile; 16, *cis*-crotonitrile; 17, butyronitrile; 18, cyclopentane; 19, toluene; and 20, *trans*-crotonitrile.

Rosetta mission by the University of Gieâen (Germany) by Herman Wollnik and coworkers with the help of Arthur Ghielmetti from the Lockheed Martin Advanced Research Center. The GC and MS instruments can be used separately or in combination. After a stepwise heating of the sample in the oven, the evolved gases will be analyzed by MS or eluted onto the chromatographic columns and analyzed by GC. GC/MS can be used if the identification of one or more GC peaks should appear questionable.

COSAC's GC subsystem

The selection and optimization of the chromatographic columns have been defined on the basis of the chemical compounds potentially present in cometary nuclei. (See Supporting Information for this article at http://pubs.acs.org/ac.) The list of the targeted compounds has been established from data provided by observations of

cometary atmospheres and the interstellar medium, in situ chemical analyses of cometary grains released from comet Halley during MS experiments of the Giotto and Vega missions, and from laboratory simulation experiments (11). The primary measurement objectives of the COSAC instrument are to analyze organic and inorganic species of the solid phase. The organic fraction is expected to include a wide range of species, from low-molecular-weight, highly volatile molecules, such as ${\rm CH_4}$, ${\rm HCN}$, ${\rm HCOOH}$, ${\rm CH_3OH}$, and ${\rm H_2CO}$, to complex molecules, such as amino acids and high-molecular-weight refractory macromolecular organics. The inorganic fraction should include molecules such as ${\rm H_2S}$, ${\rm NH_3}$, ${\rm H_2O}$, and permanent and noble gases.

We are coinvestigators of this experiment in charge of developing the columns to identify general inorganic and organic compounds. We have selected and optimized a set of five capillary columns, which cover the wide range of expected compounds and are sufficiently complementary to allow an unambiguous identification by appropriate cross-checking. All columns are custommade and developed in close collaboration with Restek and Varian Chrompack to obtain very small i.d., robust, metallic columns able to withstand the constraints of operating in space. The first column, named Carbobond, is a carbon molecular sieve porouslayer open tubular (PLOT) column (15 m long \times 0.25 mm i.d.) with a 10-µm-thick carbon porous layer bonded to the internal capillary wall. This column can efficiently separate the permanent and noble gases and C₁ and C₂ hydrocarbons in <15 min at reduced outlet column pressure and isothermally at 30 °C, which are the COSAC in situ operating conditions (12)

The detection of these families of compounds is of primary interest for understanding the origin and chemistry of comets. Indeed, the presence of hydrocarbons such as CH_4 , C_2H_2 , and C_2H_6 has recently been revealed in the comae of comets Hykutake and Hale–Bopp, with relative abundances to water of ~1%,

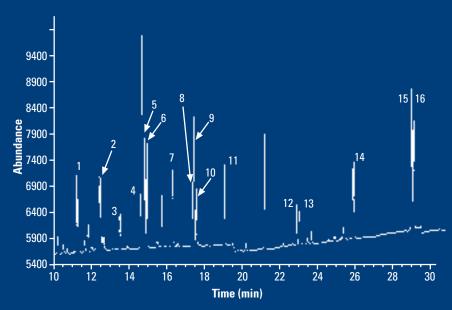


FIGURE 4. GC/MS analysis of a standard mixture of amino acids at 100 mM each.

A 10-m × 0.25-mm CP-Chirasil-Dex fused-silica WCOT column, operated in split mode (1:100), was programmed at 4 °C/min from 70 °C (held 5 min) to 170 °C with an inlet helium pressure of 19.5 kPa. Peaks: 1, ∞-aminoisobutyric acid; 2, alanine; 3, glycine; 4, ß-alanine; 5, D-valine; 6, L-valine; 7, norvaline; 8, D-isoleucine; 9, L-isoleucine + leucine; 10, 4-aminobutyric acid; 11, norleucine; 12, D-aspartic acid; 13, L-aspartic acid; 14, glutamic acid; 15, D-phenylalanine; and 16, L-phenylalanine. Adapted with permission from Ref. 21.

~0.3%, and ~0.5%, respectively. Because these molecules have also been found in interstellar molecular clouds, the detection of identical or similar relative abundances in the nucleus could confirm the close relationship between the comets and the interstellar medium (13). Likewise, for the first time, argon was detected in the comet Hale–Bopp, thus giving key information on the thermal history of comets; the trapping of argon in cometary ices depends on the ice's temperature of formation (14). Moreover, determining the abundances of noble gases and their isotopic ratios would enable researchers to evaluate the role that comets play in bringing volatiles to Earth and the other inner planets to form parts of their atmospheres (15).

Because of the fragility of their solid-layer immobilization, the PLOT columns have long been incompatible with the constraints for space travel. Consequently, only packed or micropacked columns were used in the past. However, a new generation of PLOT columns has recently been developed, using a better film-immobilization process with covalent coupling and copolymerization, which makes them able to withstand space travel, especially the vibrations during the launch.

The second column is also a PLOT column, containing a porous polymer made of divinylbenzene/ethylene glycol dimethylacrylate as a stationary phase (10 m long \times 0.18 mm i.d.), with a 2-µm-thick film. It is designed to separate the light molecules up to C₂—such as ammonia, hydrocyanic acid, formaldehyde, and methanol—within 12 min under outlet atmospheric pressure and isothermally at 90 °C (16). These compounds are fundamental for astrobiological studies of the origin, distribution, and evolution of life in the universe because they are involved in the formation of key prebiotic molecules, such as amino acids and sugars in living cells (17).

Because analyses must be performed in <17 min, a small-i.d., custom-made capillary column with a thin stationary-phase film

was specially developed. This thin film can lead to a rapid overloading of the stationary phase and give non-Gaussian chromatographic peak shapes. Nevertheless, this column has been selected because of the high priority placed on the targeted molecules and the unavailability of any other appropriate column using a liquid stationary phase. Experimental and numerical programs allowing the interpretation of complex nonlinear chromatograms are currently being developed in our laboratory (18).

The third and fourth columns of the GC subsystem are WCOT capillary columns (15 m long \times 0.18 mm i.d.) that use two complementary polysiloxane-based liquid stationary phases, containing 14% CPP/86% dimethyl and 20% diphenyl/80% dimethyl substituents with film thicknesses of 1 μ m and 1.2 μ m, respectively. These two columns are devoted to the analysis of

medium-molecular-weight organic compounds up to C_6 . The data obtained from experimental simulations in the laboratory and from in situ measurements have demonstrated large amounts of organic compounds, which belong to a wide range of chemical families, in comets. Most of these organic species could be implicated in prebiotic chemistry processes that could have occurred on Earth or elsewhere in the solar system.

Because of the large number of compounds that belong to this range of chemical species, two columns of slightly different polarity, MXT 1701 and MXT 20, have been selected to provide an unambiguous identification. Figure 3 shows chromatograms obtained for a simultaneous injection of the same sample mixture into both columns. The greater polarity of the MXT 1701 stationary phase made with CPP is clearly shown because the retention of polar compounds, such as alcohols and nitriles, is significantly better on this column even though the two columns have the same geometry and similar film thicknesses, whereas alkanes have a similar behavior on both columns. This gives the dual-column system interesting properties, from the separations viewpoint: The doublets (13 and 14, which are coeluted compounds, and 19 and 20, which are poorly resolved compounds) on column MXT 1701 are well

separated on column MXT 20. Reciprocally, compounds 9 and 15, which are coeluted on column MXT 20, are well separated on column MXT 1701. A cross-check of the data recorded on the two columns allows identification of compounds that are coeluted by generating a two-dimensional chromatographic data set.

Finally, the fifth selected column is a 100% polydimethylsilox-ane stationary-phase WCOT capillary column (10 m \times 0.18 mm i.d.) with a 0.1-µm-thick film for the analysis of heavy-molecular-weight compounds. Indeed, many heavy-weight molecules such

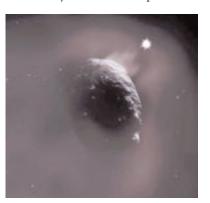
as polyaromatic hydrocarbons (PAHs) have been detected in the interstellar medium. Therefore, their presence in comets could confirm, as it did for the presence of C_1 and C_2 hydrocarbons, the interstellar origin of cometary ices and specifically the role of comets as a link between the solar system and the interstellar medium. Moreover, measurements of the dust composition of comet Halley and models have shown the probable presence of heavy refractory compounds, including polymeric species that have never been clearly identified (19).

These latter compounds could be used to support the theory of prebiotic chemistry processes. Therefore, a stationary-phase column with the thinnest possible film has been selected to reduce its retention properties and allow elution of molecules that have up to nine carbon atoms, such as trimethylbenzene, in

<15 min at atmospheric outlet pressure. Moreover, when connecting the column outlet to the vacuum (comet conditions simulation), the elution of naphthalene, the lightest PAH, is possible in <6 min at 60 °C, which is compatible with COSAC time constraints. Because this column elutes some of the same compounds as the two previous WCOT columns, the continuity of analysis is ensured and cross-checking is possible, allowing better component identification.

The GC subsystem is completed by three chiral columns designed for enantiomeric separation and developed by Thiemann and co-workers (20). Two of these columns use specific stationary phases with cyclodextrin structures (CP-Chirasil-Dex and Chiraldex), whereas the third uses an N-propanoylvaline / tert-butyl amide chemically bonded to a polysiloxane stationary phase (Chirasilval). Amino acids, which are the most important molecules in terrestrial life due to their abundance and role in biological processes, are the first molecules targeted by these columns. The possible detection of an excess of chirality could explain the exclusive left-handed origin of all the terrestrial amino acids and, therefore, indicate the seeding of life on Earth from cometary matter. Chirality of smaller molecules such as carboxylic acids—the possible degradation products of living cells will also be ascertained. These columns will

be associated with a derivatization system that uses a one-step chemical reaction process allowing the volatilization of poorly volatile compounds, such as carboxylic acids and amines, and fully nonvolatile compounds, such as amino acids. Figure 4 shows a successful enantiomeric separation of several important prebiotic amino acids, such as valine, isoleucine, aspartic acid, and phenylalanine after a one-step dimethyl-formamide/dimethylacetal derivatization process on a CP-Chirasil Dex capillary column (21).



ROSETTA AND
COSAC ARE
DESIGNED TO
COLLECT THE
FIRST DIRECT
INFORMATION
ABOUT A COMET
NUCLEUS AND ITS
ENVIRONMENT.

Table 1. Overview of the GC instruments of in situ missions.

	Detectors
арак Q (7.6 m × 0.11 cm i.d.)	Thermistor TCD (32 °C)
column coated with polymetaphenoxylene 76 cm i.d.)	MS
apak N (15.85 m $ imes$ 0.11 cm i.d.) and pair of the $ imes$ 0.11 cm i.d.); both pairs in parallel	Two thermistor TCDs in parallel
orb (2 m), one molecular sieve (2.5 m), and ed manganese in series	Three neon ionization in series
ak QS + N and one Porapak T in parallel	Helium ion and TCD, two ECDs in parallel
n molecular sieve (2 m $ imes$ 0.75 mm i.d.), one pon WCOT (14 m $ imes$ 0.18 mm i.d.), and one WCOT (10 m $ imes$ 0.18 mm i.d.) in parallel	Five MS sources (three connected to each column) in parallel
and two PLOT in parallel	One time-of-flight mass spectrometer; eight nanoTCDs in parallel
	ind two PLOT in parallel PDVB = Polydivinylbenzene

New insight

Thanks to the COSAC multicolumn GC/MS experiment, the Rosetta lander should provide the first data on the composition of a comet nucleus and its environment, which should contribute to a better understanding of the relationship between the chemistry developed in the gaseous and solid phases of a comet. However, because there are several billion comets, which have different locations and histories of formation (in particular, the number of passages near the Sun), even an exhaustive study of one comet cannot indicate their diversity. This is why several spacecraft missions, such as NASA's Discovery and Stardust programs, with in situ and sample-return investigations of comets, are planned for launch within the next decade.

Even if the name Rosetta sounds a little bit too optimistic—because there is very little hope of deciphering the mystery of our origins as Champollion did with the Rosetta stone for hieroglyphics—this mission should provide vital insight into the origins and evolution of comets. And it should help answer the fundamental questions of whether comets are the leftover building blocks of our solar system and if comets imported to Earth the starting organic ingredients and water that permitted life to emerge.

This work was supported by the Centre National d'Etudes Spatiales. We thank Helmut Rosenbauer, the principal investigator of the COSAC experiment, his team, and David Coscia.

Robert Sternberg is senior lecturer of chemistry at University of Paris 12 Vale de Marne (France) and head of the GC space instrumentation group at Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA; France). His research focuses on GC, GC/MS, and capillary columns for space-based GC/MS experiments. He is coinvestigator of the COSAC instrument. Cyril Szopa is a postdoctoral fellow at LISA. His main research interests are organic chemistry in extraterrestrial envi-

ronments and analytical chemistry for the in situ characterization of the organic composition of such environments. Claude Rodier is an assistant professor at the University of Poitiers (France). Her main research interests are organic geochemistry in sediment and water samples and the detection of organic compounds in low-concentration environmental samples. Address correspondence to Sternberg at LISA, UMR 7583, CNRS, Université Paris 7 and Paris 12, C.M.C., 61 Avenue du Général de Gaulle, 94010 Créteil Cedex, France (sternberg@lisa.univ-paris12.fr).

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