



In situ inorganic and organic analysis (Pyr/CD-GC/MS) of the Martian soil, on the Mars 2005 mission

M. Cabane^{a,*}, P. Coll^{a,b}, C. Rodier^b, G. Israel^a, F. Raulin^b, R. Sternberg^b,
H. Niemann^c, P. Mahaffy^c, A. Jambon^d, P. Rannou^a

^a*Service d'Aéronomie du C.N.R.S., IPSL, UMR 7620, Université Paris VI T15, B102, 75005 Paris, France*

^b*Laboratoire Interuniversitaire des Systèmes Atmosphériques, UMR 7583, Universités Paris VII et Paris XII, 94010 Créteil cedex, France*

^c*NASA Goddard Space Flight Center, Greenbelt, MD 20777, USA*

^d*Laboratoire de Pétrologie, Université Paris VI, T26, B170, 75005 Paris, France*

Received 15 September 1999; received in revised form 22 June 2000; accepted 18 August 2000

Abstract

In order to obtain mineralogical information, the Mars Sample Return mission, in 2003 and 2005, will include sub-surface sampling. One expects that the effects of UV radiations and oxidizing agents are attenuated at depths corresponding to the bottom of the drilled cavity. In this case, such sampling will also allow to determine if life is or has been present at the surface of Mars. We propose to perform a preliminary in situ analysis of Martian samples: SAM (*Sample Analysis on Mars*) on MSR 2005 lander. Such an analysis, performed on some parts of dedicated samples, will have the advantage of producing a ground-truth for the Earth-based analysis. Indeed, MSR 2003/2005 samples will be delivered to Earth laboratories in 2008, or 2009, depending on the duration of the quarantine, and it is not stated that some of their properties will remain unaltered during these three to 6 years. Moreover, there is a possibility that Martian sub-surface drilling delivers redundant samples: SAM could help to select, amongst the samples, which ones deserve to be sent to Earth, and, should the occasion arise, what are their unexpected peculiarities. To analyze inorganics and organics sampled at various depths, we propose to use the pyrolysis/chemical derivatization/gas chromatography/mass spectrometry technique. This experiment may be performed using techniques already developed in the frame of other planetary (ACP/HUYGENS) or cometary (COSAC/ROSETTA) missions, which can easily be adapted to the proposed mission objective, according to the three following topics: search for organics, search for inorganics and isotope characterization. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

Several billion years ago, Earth and Mars probably followed a similar evolution. The various missions to Mars (e.g. Mariner 9, Vikings 1 & 2, Mars Pathfinder and Mars Global Surveyor) largely highlighted the presence, in the past, of liquid water on the Martian surface. Liquid water requires an average temperature greater than 0°C: this requires a dense atmosphere, correlated to a greenhouse effect.

If, in the past, about four billion years ago or even most recently (Ori, 1999), the environmental conditions of these two planets were not dissimilar, it is possible that the spontaneous chemical reactions having caused the appearance of the first living forms on Earth, also occurred on Mars,

before the disappearance of water (McKay and Stroker, 1989).

A way of studying this assumption is through research of prebiotic chemistry. It is in particular in this framework that “Mars Sample Return” missions were decided, the purpose of which is principally to recover samples of the Martian ground, then to bring them back on Earth for analysis. These analyses will have as a finality to determine the mineralogical and chemical composition of these samples, in order to study the Martian geology, and possible past or present biology. During the 1970s, the NASA Viking mission did not find any biological activity, and the only positive answers of the experiments were finally attributed to the chemical reactivity of the soil (see for example Kieffer et al., 1992 and McKay, 1997).

The Martian exploration program slowed until ‘Martian’ meteorites were identified on Earth. Analysis of gases enclosed in these rocks, and their comparison with the atmospheric analysis of Viking, made it possible to suppose

* Corresponding author. Tel.: 33-1-4427-4970; fax: 33-1-4427-3776.
E-mail address: michel.cabane@aero.jussieu.fr (M. Cabane).

their Martian origin. In some of these meteorites, for example ALH 84001, carbonates were identified, as well as organic matter (McKay et al., 1996). It is difficult to determine if this matter comes from Mars, or if it is a contaminant from Earth (see discussion on <http://cass.jsc.nasa.gov/lpi/meteorites/life.html>). But if this organic matter comes from Mars, one may ask the question: why did Viking experiments fail to detect it?

The most consistent explanation for Viking's failure to detect organic molecules, lies on photochemically produced oxidants, which originate in the atmosphere and diffuse into the regolith, and are a potential source of degradation of organics, including bioorganics. Bullock et al. (1994) suggested that hydrogen peroxide, H_2O_2 , produced from atmospheric water vapor by UV radiations, may diffuse into the soil before its destruction by UV. These calculations were carried on by Zent (1998), who showed that the most likely scenarios for regolith gardening by impacts, onset of oxidizing conditions and oxidant extinction depth, yield estimates of no more than a few meters for the 50% degree of oxidation depth. Another source of oxidation could be peroxides produced from the adsorbed H_2O on the soil particles (Huguenin et al., 1979). Processes of direct degradation of organics by solar UV also exist, but are limited to first 10 μm . It is important to notice that recently Benner (2000) proposed that some organic polymeric compounds resulting from the organic matter degradation could be present on the Martian surface or sub-surface, but that the experimental conditions of Viking's pyrolysis were not compatible with their detection. In consequence he assumes the presence of heavy organic molecules and organic salts on the surface and in the Martian underground.

It thus appears essential to go back to Mars, to seek organic compounds, which may reveal some signs of a present or past biological activity. It is essential to have access not only to surface, but also to sub-surface samples, to a depth where the possible effect of UV radiation on the chemical indicators of life is negligible, as well as the concentration of oxidizing agents. An analysis of inorganics will make it possible to obtain a better knowledge of mineralogy and quantity of water contained in the ground. The knowledge of the quantity of adsorbed H_2O will allow to check the models and, together with the analysis of carbonates and other salts, to have a better understanding of the past Martian climate. Of course, the search for organic molecules, from the simplest hydrocarbons to the macromolecules, will lead to a better comprehension of the prebiotic conditions, or even of the life, which could exist in the past. An isotopic study of the samples will supplement this investigation. It will allow in an unquestionable way to conclude on the existence, past or present, of a biological activity on Mars, especially in the case of narrow isotopic range (Rothschild and Desmarais, 1989).

The interest of SAM (Sample Analysis on Mars), an experiment involving the in situ analysis of samples from the Martian sub-surface is, obviously, that it may

be used as point of reference with respect to the subsequent analyses on Earth. Indeed the sampling, in 2003 and 2005, will be followed by a conditioning phase, then a multi-stage transfer towards the Earth. Samples will be then recovered on Earth, and possibly decontaminated before their analysis in laboratory, in 2008–2009. They will therefore be confronted with some risk of contamination, as well as environmental stress due to potential changes in atmosphere composition, including physical (variation in pressure and temperature) or chemical. The in situ immediate processing will make it possible to analyze samples of surface and sub-surface not having undergone contamination, which will be an overview preceding the finer analyses carried out on samples brought back to Earth by MSR.

All the samples obtained from the Martian sub-surface by drilling will not be retrieved, and SAM (Sample Analysis on Mars experiment) can contribute to a preliminary selection with respect to the top priority of the mission. In addition, in situ analysis will act synergistically with the Earth-ground laboratories to analyze the Martian samples. These first data will be able, indeed, to give clues leading to optimization of the techniques of analysis which will be used in 2008/09. Furthermore, such results may play a key role in the selection of the 2007 landing site. Obviously, a fruitful option would be, for us, to have the occasion of analyzing, as soon as possible after its collection, part of the sample which will be brought on Earth, using the analytic techniques that we have developed in our laboratories.

2. Rationale

2.1. Targets of the Sample Analysis on Mars

2.1.1. Search for inorganic compounds

As emphasized by the ESA Exobiology-science team (1999), the study of mineralogy and inorganics as a function of depth will provide data to model a water concentration profile. This is a key for studying the potential for extant life in the present Martian sub-surface. Data regarding the concentration of H_2O and amount absorbed in the regolith will also permit a better understanding of some aspects of the hydrological cycle.

Determination of the mineralogical composition of the inorganic phase (hydroxides, phyllosilicates) needs the knowledge of water release during its heating. In the same way, it is significant to obtain the abundance of carbon dioxide, CO_2 , in the ground (presence of carbonates), and also, that of the species such as $NO_2^-/NO_3^-/N_xO_y$ (presence of nitrogen oxides), SO_2/SO_3 (presence of sulphates). The temperatures where the inorganic materials release their structural H_2O , CO_2 and SO_2 , etc. can be of a great help for a better identification (see Anderson and Tice, 1979; Clark, 1982).

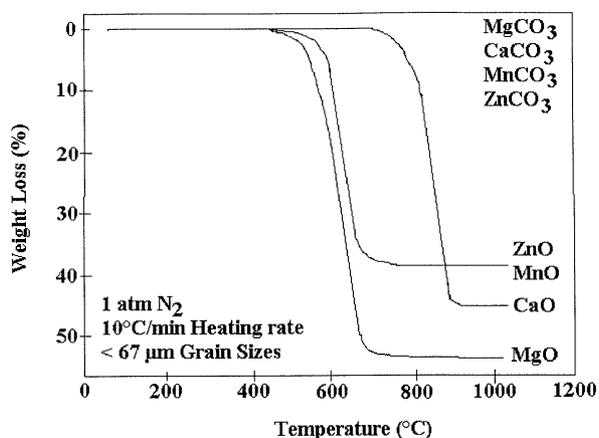


Fig. 1. The thermal stabilities of mineral phases and their volatile release profiles were studied by conventional thermogravimetric analysis. Here are presented decomposition of magnesite, calcite, rhodochrosite and smithsonite at heating rates of up to 10°C/min. Pyrolysis experiments results, at heating rates much faster, are also available in the original article (adapted from Kotra et al., 1982).

The analysis of the duricrust should thus make it possible to understand the vertical migration of salts in the ground, and highlight the last climatic cycles: carbonates, sulfates and nitrates are witnesses of periods of sedimentation, the deposits of carbonates, for example, should be close to surface if the Martian atmosphere were mainly thick in the course of time. Furthermore, clays, phosphates and carbonates, inter alia, are minerals resisting the chemical weathering, and, thus, can conceal organic materials resulting from periods of biological activity on Mars.

Thermal stabilities of mineral phases and volatile gas release profiles of the suggested volatile-rich materials of the Martian regolith were studied in detail. Thermal analysis, combined with mass spectrometry, was applied to the study of the behavior of carbonates, sulfates, hydrates and clays. They indicate that these techniques are useful in the preliminary mineralogical characterizations of volatile-rich minerals. Fig. 1 shows the decomposition of carbonates under heating (CO₂ release). However, the development of such technique for space exploration needs care, because many factors affect volatile release (pressure for example, see Kotra et al., 1982). The samples need to be pyrolysed to temperatures above 500°C, which will permit a reliable CO₂ release from carbonates near these temperatures, and other compounds at higher temperatures up to 1000°C. These temperatures were not reached by the analysis carried out on the Viking Mission. Moreover, the use of dedicated temperature steps will permit to assert the temperatures at which structural gases will be emitted, hence an assistance for mineralogical interpretations.

2.1.2. Search for organic compounds

The Martian environment is strongly oxidizing, consequently, the abiotic formation of organic compounds by atmospheric chemical processes is improbable. Thus,

the extra-Martian matter importation by the impact of carbonaceous meteorites constitutes the principal abiotic source of organic compounds (surface and near underground). Provided that one can differentiate between abiotic origin and bio-origin, the organic carbon detection in the Martian underground would allow the highlighting of processes related to life (ESA Exobiology-Science Team (1999), McKay and Stroker, 1989).

On Earth, some primary biopolymers (e.g. proteins and polysaccharides), constituents of dead organisms, undergo degradation and condensation processes, generating complex and chemically stable macromolecular materials. These species, amorphous condensed aggregates, made up mainly of aliphatic and aromatic groups, are called kerogens. Moreover, some other biopolymers (rich in lipids) evolve directly into kerogens. Such compounds represent the majority of the organic sedimentary matter and their chemical composition is a function of the thermal history. Sediments also contain stable organic compounds, such as lipids, that can support the processes of deterioration, or are the result of the thermal degradation of the kerogens. Many of them are regarded as biomarkers, because of their chemical structure and/or their carbon isotopic composition. While being based on the experience gained on Earth on the microbial origin of organic compounds, it is possible to distinguish some characteristics of the organic matter, making it possible to identify its biological origin, namely:

- compounds (present or derived from pyrolysis), with some structure characteristic of an origin requiring biosynthesis (e.g. terpenoids, steroids, etc.);
- homolog series of components, present in the sample or in pyrolysis products, presenting a non-random distribution of the number of carbon atoms (straight chain hydrocarbon, etc.);
- depletion of ¹³C in the isotopic composition of the collected organic matter, of its fragments, or of its pyrolysis products (cf. isotopic analysis).

The search for volatile organics of low molecular weight is also significant. The identification of elementary compounds like CH₄ or H₂S in samples of the near underground, in spite of the strongly oxidizing environment of Mars surface, could also be a sign of a biological activity in this zone. In such an environment, the selection of the target organic molecules will have to take into account the relative chemical stability of these compounds. In particular, among the blocks constituting the bio-macromolecules, amino acids are relatively stable, purines are more stable than pyrimidine, nucleotides and their sugars are not.

On these bases, the priority targets are as follows:

- *volatile compounds of low molecular weight*: CH₄ and other C₁ or C₂ hydrocarbons, H₂S, carboxylic acids;

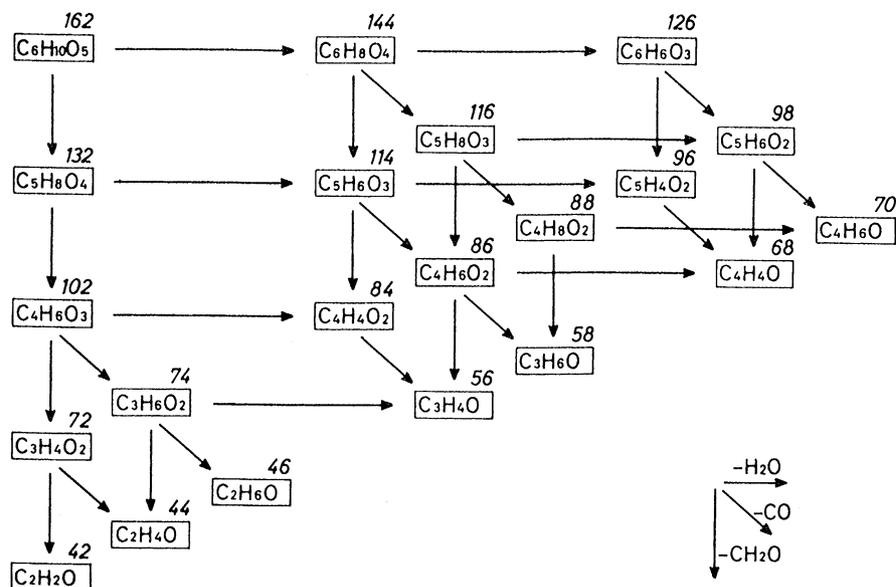


Fig. 2. Example of some pyrolytic degradation pathways proposed for hexose polymers. Hexose gross formula is $C_6H_{10}O_5$, its molecular mass is 162 D. Here the different fragments that its pyrolysis produces, with their relevant masses are shown. On the right bottom of the scheme, the mechanism processes associated with the fragmentation, e.g. a horizontal arrow corresponds to a water loss (adapted from Meuzelaar et al., 1982) are represented.

- *compounds of low molecular weight*: other hydrocarbons (chains ramified or not, aromatic, etc.), carboxylic acids, alcohols, amino acids, purins;
- *macromolecular compounds*: kerogens, oligopeptides.

2.2. Tools planned for the Sample Analysis on Mars

2.2.1. Pyrolysis

Low molecular weight compounds and some of the medium molecular weight compounds could be detected (e.g. mass spectrometry, gas chromatography, see below) by heating the sample at moderate temperatures. At higher temperatures (above 500°C), pyrolysis of the sample is a powerful tool for the analysis of non-volatile compounds of low thermal stability, in particular organic compounds of high molecular weight, such as macromolecules or oligomers. In fact, the thermal pulse fractures the bonds between separate entities to produce recognizable molecular sub-units (Irwin, 1982). Analysis of the gaseous mixtures that are produced from the pyrolysis of a given organic compound provides a “Fingerprint” (nature and abundance (GC-MS) of released gases), which can be compared to laboratory data bases. Thus, from this fingerprint, we can identify the complex molecules which constitute the pyrolysed samples. As an example, Fig. 2 gives the interpretation of a pyrogram obtained from pyrolysis of hexose polymers (Meuzelaar et al., 1982).

2.2.2. Chemical derivatization

Chemical derivatization allows better sample analysis as it increases analyte volatility, improves chromatographic characteristics of an analyte by decreasing its polarity and/

or increasing the detector sensitivity of the target analytes (Wells, 1999; Blau and Halker, 1993).

Moreover, some compounds, which could be present in the soil sample, may be too refractory to be easily analysed (Benner, 2000), consequently, there is no signal delivered as a result of the pyrolysis phase. In this case, the chemical derivatization (CD) of such constituents is complementary to pyrolysis. Chemical derivatization can cause cleavage or “chemolysis” of certain functional groups so that compounds could be easily recovered and transformed, in a chemical reactor, into volatile compounds, able to be directly analysed. Conversely, another possibility is that the compounds are thermally fragile, in that case the heating of the material will give rise to elementary molecules (O_2 , H_2O , etc.) that are not of significant interest. In the same way, the derivatization of these compounds will help to preserve the structural information. Examples of chemical reactions used for derivatization are shown in Fig. 3.

2.2.3. Isotopic analysis

Isotopic ratios are a powerful tool for the identification of chemical biomarkers. SAM will be able to propose such isotopic analysis complementary to physicochemical measurements, helpful to characterize the organic and inorganic phases of the analyzed samples.

On Earth, the depletion in ^{13}C , resulting from Calvin photosynthesis cycle, is an unambiguous signature of a biological activity. Other systems, where the photolysis occurs, enable carbon fixing in the form of ^{12}C , but to a lesser extent. The $\delta(^{13}\text{C})$ of an average biomass is lower by 20–30% than that of inorganic carbon. On Earth, this shift remained

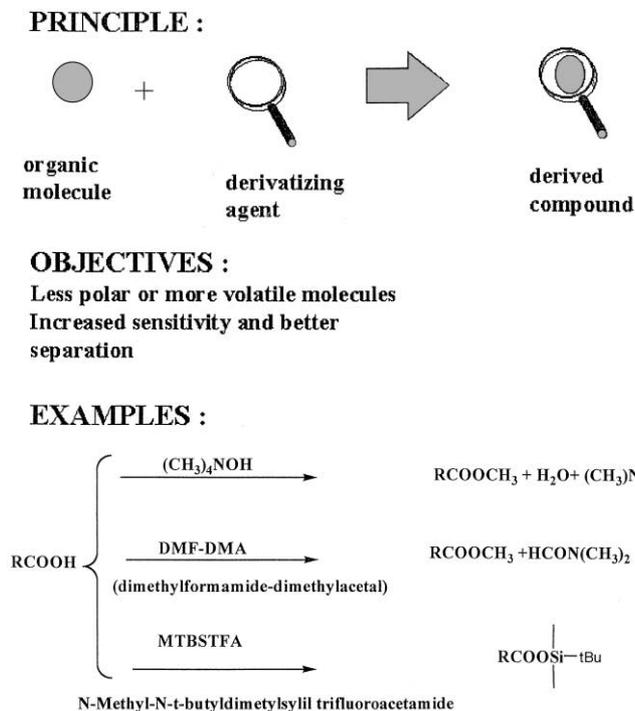


Fig. 3. Illustration of chemical derivatization (CD) principle and examples of one-step reactions commonly used in laboratory that could fulfill all our requirements. The carboxylic acid on the left side of the reaction scheme is derivatized using three different reactions. This leads, from top to bottom, to different esters, which can be easily analyzed by conventional means.

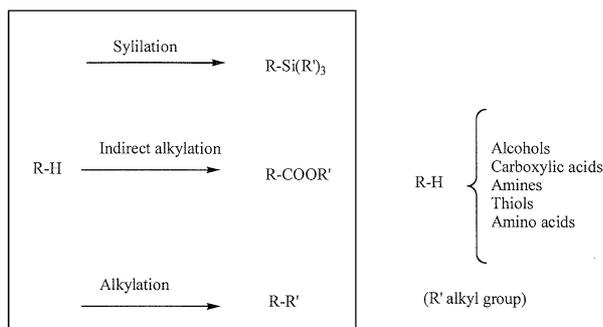


Fig. 4. Types of derivatization studied for prebiotic molecules: derivatization reagents are employed to replace a labile hydrogen atom, attached to a heteroatom, with a less polar, non-volatile group.

constant throughout the history of the planet. However, it is not very probable that the Calvin photosynthesis cycle exits or took place on Mars, and another type of metabolic scheme would lead to another isotopic fractionation. For example, on Earth, the isotopic fractionation of carbon in atmospheric CO_2 depends on the trophic level and the medium of CO_2 collecting (Tysson, 1992).

The first question to elucidate in the case of Mars is the determination of the isotopic composition of the source of carbon. Indeed, the transition of carbon dioxide CO_2 , or

carbonates, to a reduced phase (organic matter) is always accompanied by an isotopic fractionation, the process being biological or not. On Earth, one knows rather well the processes — physical and chemical (including biological) — which can intervene, and it makes it possible to get information of such isotopic measurements, nevertheless, it is not the same in the case of Mars. The isotopic composition will be in this case one of the elements necessary to the conclusion, but, alone, it would be insufficient. Thus, the coupling with the chemical analysis presented above will be of great importance (see review by Rothschild and Desmarais, 1989).

In the same way, it will be also possible to foretell a biological activity by the isotopic analysis of the element sulfur. The terrestrial biosphere contains significant amounts of sulfur, and its isotopic signature in various states of oxidation makes it possible to highlight biologically controlled processes, generally in sedimentary environments at low temperature. But as in the case of carbon, we do not have the same knowledge on the Martian environment as what we know of Earth. Consequently, a complete comprehension of the cycle of Martian sulfur, and thus of a biological influence in this cycle, requires a study of isotopic abundances of sulfurated species, both oxidized and reduced.

One may add that, in spite of the difficulty in exploiting these data, the determination of isotopic ratio $^{15}\text{N}/^{14}\text{N}$ will permit to highlight biological activities in the analyzed samples; besides, the alteration of the soil at a given period of time leaves traces in the isotopic composition, and the study of ratio D/H , as well as the study of oxygen isotopes, can be of a particular interest.

In conclusion, the isotopic analysis, that SAM will be able to perform, will be an essential complement for the physicochemical characterization of the organic and inorganic phases of the analyzed samples.

3. Analysis methodology

To analyze inorganic and organic compounds from Martian surface samples and sub-surface samples, we propose an experiment based on the Pyr/CD-GC/MS principle. The assets of such a technique are multiple. Heating and pyrolysis of the sample up to $T = 1000^\circ\text{C}$ and chemical derivatization ensure the extraction of information on the molecular structure of compounds present in the sample. Analysis of the gases produced at the end of these processes may be performed using mass spectrometry. This technique is extremely well adapted to planetary exploration, because all atoms and molecules having a mass included in the range of sensitivity of the mass spectrometer (1–300 amu for example) will be detected. Of course the identification of the species is even more precise when this tool is coupled with a system of chromatography, which lets gases elute at times depending on the characteristics of

their constituting atoms or molecules. In this case the coupling constitutes one of the most powerful tools available for the analysis of complex gas mixtures, and is also very effective for separations of couples of isotopes: $^{13}\text{C}/^{12}\text{C}$, D/H, $^{15}\text{N}/^{14}\text{N}$, $^{34}\text{S}/^{32}\text{S}$, etc.

Chemical sensors based on GC and MS instrumentation have already been used in atmospheric probes of surface landers for analyzing extraterrestrial environments, including the analysis of Venus and Mars surface materials (Biemann et al., 1997). The Aerosol Collector Pyrolyser ACP experiment (Israel et al. 1997, 1999) on Huygens probe (Cassini- Huygens Mission, 1997–2004) uses such technique to analyze the organic aerosols in Titan's atmosphere, connected with the GCMS experiment (Niemann et al., 1997). In this frame, new instrumentation involving Pyr-GC-MS techniques and using the heritage of Huygens is currently under development for space application, in particular for in situ analysis of cometary nuclei (COSAC and MODULUS experiments on ROSETTA (Rosenbauer et al., 1999), CHARGE experiment on CHAMPOLLION (Mahaffy et al., 1999). Moreover, one innovative method, complementary to the preceding ones, the chemical derivatization, already under consideration on COSAC, will be developed on SAM.

Our project of in situ analysis (SAM: Sample Analysis on Mars) is a device that is divided into three parts: the first is included in the lander common delivery system (soil sample delivery), and the two other parts of the experiment, the pyrolyzer/chemical-reactor and gas-chromatograph/mass spectrometer are, respectively, applied to the sample preparation and the sample analysis.

3.1. Sample preparation step

Depending on the experiment sequence, two gas mixtures will be generated

From the thermal decomposition of the soil in an oven (pyrolysis), we propose to provide analysis of inorganic and organic compounds. It consists of sample heating using micro-ovens. At each temperature level, a gaseous phase is obtained from vaporization (with conservation of the original molecular structure) or by cracking (and then fragmentation at high temperature). This technique will be applied to mineral compounds, in our case at temperatures less than 1000°C (cf. Fig. 1), and to organics that will be pyrolyzed in the same temperature range (cf. Fig. 2).

The complementary technique is chemical derivatization. Its main goal is to allow analysis of refractory compounds and thermally fragile compounds of biological or prebiotic interest, from a chemical processing of the soil in a reactor. Its principle is to induce a chemical reaction between a determined chemical group of a molecule and a reactant (cf. Fig. 4). This reaction has to be universal for functional groups existing in organic matter (derivatization of alcohols, carboxylic acids, aldehydes, etc.).

3.2. Sample analysis

The gaseous phases obtained from the “sample preparation” step are then transferred to the analyzer, a gaseous phase chromatograph coupled with a mass spectrometer. The diverse species, constituents of the analyzed gaseous sample, are then detected following three different modes:

- (1) GC mode: the various compounds of the gas mixture are separated by chromatographic columns, quantitative measurements of eluted gases are performed by universal detectors (e.g. thermal conductivity detectors, flame ionization detectors, helium ionization detectors, etc.).
- (2) MS mode: the analysis by a mass spectrometer is performed without any preliminary compound separation. This mode is specifically devoted to “in-time” analysis of gaseous compounds obtained in the ovens. Another system, limited to quantitative analysis, could be added. It could be made using catharometer detectors, disposed at oven exits, that could determine the gas production as a function of the oven internal temperature.
- (3) GC-MS mode: separation on chromatographic columns and measurement using the mass spectrometer. This technique allows to solve ambiguous identification cases (coelution of isomers, etc.).

Two types of data are then obtained: one is delivered by GC nano-detectors associated with columns (thermal conductivity detectors, TCD, and helium ionization detectors, HID), the other by MS. Their processing allows the identification of each compound (respectively, due to their fragmentation and their elution time) and their quantification (respectively, due to their m/z signal intensity and their peak surface).

4. Technical description of SAM experiment

A preliminary design of the SAM experiment is presented in Fig. 5. The instrument consists of five main subsystems:

4.1. Cells of sample preparation

The sample preparation device is made of four pyrolysis micro-ovens and of two derivatization reactors. Each of these six cells is devoted to receive a solid sample deposited by the drilling system of the lander. A common sample delivery system (not included in this proposal) will provide the samples to the oven.

First, each micro-oven is specific for samples coming from one drilled area, from a controlled depth. A preliminary number of three micro-ovens is envisaged, considering only one drilling point at three different depths

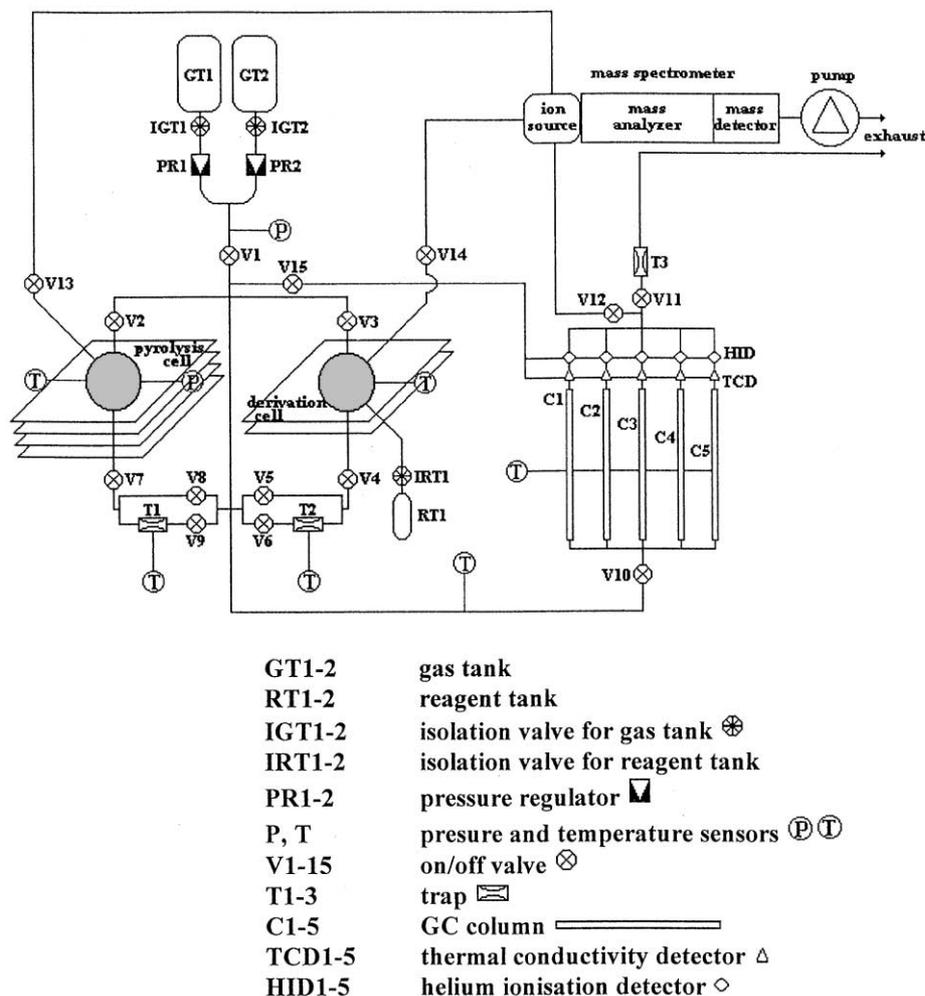


Fig. 5. SAM instrument scheme: this device is divided into three parts: the first is included in the lander common delivery system (soil sample delivery, not presented on this figure), and the two other parts of the experiment, the pyrolyzer/chemical reactor (the two cells on the left part of this figure) and gas-chromatograph/mass spectrometer (on the right part of this figure) are, respectively, applied to the sample preparation and the sample analysis.

(e.g. surface, 0.5 and 1.5 m). The fourth micro-oven will be used for tests between each analysis (background signal). Then it will permit to determine spurious influences, resulting from the transfer circuit of gaseous phases between different analyses.

Each pyrolysis micro-oven is heated in a controlled way between the temperature of Mars environment and 1000°C. The emission of volatile compounds and adsorbed molecules (including adsorbed or bounded water) results from the lowest temperature steps (from –100 to 250°C). The medium temperature steps (250–700°C) are correlated with emission of lower bounded molecules, organics cracking and CO₂ liberation from carbonates. The higher temperatures (up to 1000°C) are necessary for SO₂ and NO₂ emission, coming, respectively, from sulfates and nitrates (Desaunettes, 2000).

The two reactors are devoted to sample processing by derivatization, with a priority for the deepest samples: consequently, complex organic molecules that are non-volatile

and/or thermally fragile, and that present a biological or prebiotic interest can be analyzed. They are polyoxymethylenes, HCN polymers, amino acids, pyrimidic bases, and polyaromatic hydrocarbons.

The reactors are connected to a reservoir of reactant and will be thermally regulated to almost 250°C, this maximum temperature taking into account the reaction temperature and the evaporation temperature.

Constraints on this study are:

- (1) one-step chemical reaction (only one reagent) during the derivatization phase;
- (2) specificity of the target molecules/reagent;
- (3) quantitative dependence of the reaction to the sample nature;
- (4) kinetic dependence of the reaction to the temperature.

Due to spatialization constraints, the one-step reactions using only one reactant are studied (Rodier et al, 2000).

The usual pre- and post-derivatization step (respectively, extraction and then purification before analysis) are equally studied.

4.2. Transfer circuit

This circuit allows fluids circulation between the different parts of SAM experiment. It consists of low-diameter tube, in which gas flows are controlled by isolation valves.

4.3. Gas chromatograph

Gas chromatography allows, under suitable conditions, the separation of complex mixtures of hydrocarbons, alcohols, nitriles, carboxylic acids and other gases. The sample preparation step provides a mixture of gases, which is introduced into a carrier gas stream that flows continuously through the column. Each component, in the ideal case, elutes from the column outlet at a different time. A detector at the outlet gives a signal related to the quantity of each eluted compound.

Several chromatographic columns with different properties operate in parallel, to cover the range of Martian soil compound diversity. The choice of using five columns working in parallel (Fig. 5) is due to the need of analyzing simultaneously a potential great number of organic and inorganic compounds. Each column is connected upstream to an helium reservoir and downstream to the detectors.

The compound detection is realized using two “universal” detectors in series (universal means that they give a signal for each molecule present in the carrier gas). The first detector is a TCD (thermal conductivity detector) with a large dynamic range, that allows the detection of ratios from some percents to few ppm. A miniaturized TCD (nano-TCD) using “solid-state” technology could be used in spatial environment. To obtain a better sensitivity, an helium-ionization detector (HID) is located downstream each TCD. The HID is a “universal” detector, ppb sensible. It presents a good linearity on a dynamic of 10^5 .

At the outlet of the chromatographic columns, a helium flow of few ml/min exits to the environment of the instrument during the analysis. To avoid the perturbation of the local atmosphere, mineral and organics fractions included in the helium flow will be trapped in a non-reversible system. Upstream to columns a second system of reversible trapping is inserted in the circuit, to avoid pollution by the non-injected fraction of the sample. After the analysis sequence, these compounds are extracted by heating the trap to 250°C.

4.4. Mass spectrometer

Mass spectrometry is ideally suited for this exploration mission, as all atoms and molecules within the mass and sensitivity range of the mass spectrometer will be

detected, and no previous knowledge of the composition of the samples is required. A more accurate identification of species is achieved with a gas chromatographic system coupled with mass spectrometer. GC-MS-coupled systems are among the most powerful analytical tools available for quantitative chemical analysis of many types of compounds, especially of complex gas mixtures, and will be also very efficient for the separation of isotopes couples: $^{13}\text{C}/^{12}\text{C}$, D/H, $^{15}\text{N}/^{14}\text{N}$, $^{34}\text{S}/^{32}\text{S}$, etc. (Sternberg and Szopa, 1999; Szopa and Sternberg, 1999).

The MS sub-system will be used in real time during the pyrolysis steps by admission, in their ionic source, of a small amount of the gaseous phase produced in the cells. Such a mode, called MS direct, allows one to obtain mass spectra quasi immediately after the production of compounds in the gaseous phase. We can determine precisely the desorption temperature of the compounds, that is related to the mineral nature of samples. The MS direct mode will also perform analysis that GC-MS mode cannot carry out, for example in case of unstable compounds or of compounds able to condense in the GC system. Further, the MS will be able to work downstream the chromatographic columns and their detectors. Taking into account the use of five chromatographic columns in parallel, the GC mode would be powerful enough to realize the identification of each compound present in the gaseous mixture. Nevertheless, the GC-MS mode is useful for the identification of complex signals from the detectors (simultaneous elution of several molecules) and for analyzing samples resulting from chemical derivatization.

4.5. On board electronics

On board electronics control the sequences of valves opening and closing, acquire and control pressure and temperature data, and control the physical parameters of traps. They manage also the program including temperature and steps of pyrolysis, reactant duration and temperature of derivatization, and GC/MS analysis program. All the procedures are established before the Mission launch, and then electronics manage the complete analysis.

5. Conclusion

The main objective of this experiment is to carry out an in situ characterization of the mineral composition and organics presence in the Martian surface and sub-surface. This experiment will be complementary to the Mars Sample Return Mission, in terms of sample selection, anticipation of Earth-based results and ground-truth.

This project benefits from our experience in such in situ analysis, as the ACP experiment in the Huygens mission (target object: Titan), and COSAC experiment from Rosetta mission and CHARGE experiment from Champolion/ST4 mission (target objects: cometary nuclei).

This project is composed of two stages: sample preparation, and then sample analysis. The sample preparation is based on the complementarity of two techniques, one of them (derivatization) very innovative. These are, on the one hand, pyrolysis (Pyr), devoted to the identification of molecules of heavy molecular mass, and on the other hand, chemical derivatization (CD), devoted to identification of molecules of lower molecular weight, by transformation of some of them, unable to be analyzed by classical GC, into less polar and more volatile compounds.

The sample analysis is carried out by using classical analytical techniques as gas chromatography (GC), mass spectrometry (MS), and GC-MS coupling, adapted to the specificities of the Martian environment.

This project is supported by three programs of *Research and Development* sponsored by CNES related to both phases: sample preparation and analysis. They consist of:

- (1) study and miniaturization of a high-temperature pyrolysis oven;
- (2) selection and spatialization of a method of chemical derivatization;
- (3) evaluation of new nano-technologies concerning chromatographic detectors.

Acknowledgements

The authors want to deeply thank David Coscia for his help on SAM schemes, and Yves Bénilan and Cyril Szopa for their general help.

References

- Anderson, D.M., Tice, A.R., 1979. The analysis of water in the Martian regolith. *J. Mol. Evol.* 14, 33–38.
- Benner, S.A., 2000. The missing organic molecules on Mars. *Proc. Natl. Acad. Sci. USA* 97, 2425–2430.
- Biemann, K., et al., 1997. The search for organic substances and inorganic volatile compounds in the surface of Mars. *J. Geophys. Res.* 82, 4,641–4,648.
- Blau, K., Halker, J.M. (Eds.), 1993. *Handbook of Derivatives for Chromatography*, 2nd Edition. Wiley, Chichester.
- Bullock, M.A., Stoker, C.R., McKay, C.P., Zent, A.P., 1994. A coupled soil-atmosphere model of H₂O₂ on Mars. *Icarus* 107, 142–154.
- Clark, B.C., 1982. Analysis and interpretation of Viking inorganic chemistry data (Mars data analysis program). Final Report, Martin Marietta Aerospace, Denver.
- Desaunettes, B., 2000. A micro-oven for pyrolytic analysis EPSILON-AER Technical Report, Labège, France.
- ESA Exobiology-Science Team, 1999. The search for life on Mars. ESA SP-1231.
- Huguenin, R., Miller, K.J., Hartwood, W.S., 1979. Frostweathering on Mars: experimental evidence for peroxide formation. *J. Mol. Evol.* 14, 103–132.
- Irwin, W.J., 1982. *Analytical Pyrolysis: A Comprehensive Guide*, Chromatographic Science Vol. 22. Marcel Dekker, New York.
- Israel, G. et al., 1997. The aerosol collector pyrolyser (ACP) experiment. ESA SP-1177, 59–84.
- Israel, G., Cabane, M., Coll, P., Coscia, D., Raulin, F., Niemann, H., 1999. The Cassini-Huygens ACP experiment and exobiological applications. *Adv. Space Res.* 23, 319–331.
- Kieffer, H.H., Jakosky, B.M., Snyder, C.W., Matthews, M.S. (Eds.), 1992. *Mars*. University of Arizona Press, Tucson, AZ.
- Kotra, R.X., Gibson, E.K., Urbancic, M.A., 1982. Release of volatiles from possible Martian analogs. *Icarus* 51, 593–605.
- Mahaffy, P.R. et al., 1999. The Champollion cometary molecular analysis experiment. *Adv. Space Res.* 23, 349–359.
- McKay, C.P., 1997. The search for life on Mars. *Origins of Life and Evolution of the Biosphere*, 27, 263–289.
- McKay, C.P., Stoker, C.R., 1989. The early environment and its evolution on Mars: implications for life. *Rev. Geophys.* 27, 189–214.
- McKay, D.S. et al., 1996. Search for past life on Mars: possible relic viogenic activity in martian meteorite ALH84001. *Science* 273, 924–930.
- Meuzelaar, H.L.C., Haverkamp, J., Hileman, F.D., 1982. *Pyrolysis Mass Spectrometry of Recent and Fossil Biomaterials*. Elsevier, Amsterdam.
- Niemann, H. et al., 1997. The gas-chromatograph mass spectrometer aboard Huygens. ESA SP-1177, 85–107.
- Ori, G.G., 1999. Variability of surface processes on Mars and their implications on the geological and climatic history. *Bull. Am. Astron. Soc.* 31 (4), 1134.
- Rodier, C. et al., 2000. Detection of amino-acids from Mars by chemical derivatization coupled to gas chromatography: in-situ and laboratory analysis. *Adv. Space Res.* in press.
- Rosenbauer, H., Fuselier, S.A., Ghielmetti, A. et al., 1999. The Cosac experiment on the lander of the Rosetta mission. *Adv. Space Res.* 23, 333–340.
- Rothschild, L.J., Desmarais, D., 1989. Stable carbon isotope fractionation in the search for life on early Mars. *Adv. Space Res.* 9, 159–165.
- Sternberg, R., Szopa, C., 1999. Gas chromatography in space exploration: capillary and micropacked columns for in situ analysis of Titan's atmosphere. *J. Chromatogr. A* 846, 307–315.
- Szopa, C., Sternberg, R., 1999. Gas chromatography for in situ analysis of a cometary nucleus: characterization and optimization of diphenyl/dimethylpolysiloxane stationary phase. *J. Chromatogr.* 863, 157–169.
- Tyson, R.V., 1992. *Sedimentary Organic Matter*. Chapman & Hall, London.
- Wells, R.J., 1999. Recent advances in non-silylation derivatization techniques for gas chromatography. *J. Chromatogr. A* 843, 1–18.
- Zent, A.P., 1998. On the thickness of the oxidized layer of the Martian regolith. *J. Geophys. Res.* 103 (E13), 31,491–31,498.