LABORATORY STUDIES ON COMPLEX ORGANIC MOLECULES ON MARS
PART 1 - RATIONALE

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ABSTRACT

The search for organic molecules and traces of life is the future perspective of several missions to Mars. In order
to know what those mission should be looking for, laboratory experiments under simulated Mars conditions
are necessary. Especially since the Viking mission did not find any traces of organic compounds in the Martian
soil. In this paper the history of the search for life on Mars and the context of our laboratory studies [1], are
described. Furthermore it gives a short description of the experiments. This paper is the first part of a series
of three papers. The second paper will describe the experiments and methods [2], the third paper will be a
status report [3]. Both the second and the third paper can be found in the proceedings of the Second European
Workshop on Exol/Astrobiology, ESA Special Publication SP-518.

1. THE HISTORICAL PERSPECTIVE

One of the fundamental questions in Solar System exploration has always been if there is life beyond the
Earth and especially on Mars.

In 1892 Camille Flammarion published his ideas on life on Mars in a book called, "La Planète Mars et ses
Conditions d'Habitation". It contained a compilation of all credible telescope observations of Mars carried out
until then, and Flammarion's main conclusion was that Mars is obviously habitable. A few years before in 1877
Giovanni Schiaparelli had already published his apparent "discovery" of canals. Infected by Schiaparelli's "discoveries"
Percival Lowell stated that the canals could be nothing else than the result of the work of very intelligent beings. He confirmed this with observations showing that the canal network was too regular to be natural, concluding they should have been created by a species more advanced than humans. Furthermore he concluded that the polar caps seen on the planet could be nothing else than water ice and that the dark spots seen along the canals were growth of vegetation. In 1961 some of Lowell's ideas appeared to be still alive when Vaucouleurs published his 'The Physics of the Planet Mars'. He wrote that Mars had a
85 mbar nitrogen atmosphere, is cold, but with a tolerable surface temperature, has seasonal changes probably
due to vegetation, and that the polar ice caps are not composed of frozen CO2 but of water-ice.

In 1960 a new era in the exploration of Mars begun. The Soviet Union was the first country to send a spacecraft,
Mars 1960A, to Mars. Unfortunately this mission and seven of its successors failed, making US Mariners 4, in
1965, the first mission to reach Mars. Mariner 4 showed that Mars had a cratered, rust-coloured surface, with
signs of ancient presence of liquid water on some parts. From its data a surface atmospheric pressure of 4.1 to
7.0 mbar could be estimated, no magnetic field was detected. Mariner 6 and 7, launched in 1969, showed that
Mars' south polar cap is predominantly composed of CO2, and that the atmospheric surface pressure lays
between 6 and 7 mbar. In 1971 the Soviet Union sent two spacecraft to Mars, Mars 2 and 3. Although the
landers failed, the orbiters sent back new data that enabled creation of surface relief, temperature and
pressure maps, and gave information on the Martian gravity and magnetic fields. Mariner 9, launched too in
1971, made the first detailed images of the volcanoes, Vales Marineris, the polar caps and the moons Phobos
and Deimos. It also revealed new data on global dust storms, the tri-axial figure of Mars, the rugged gravity
field as well as evidence for surface Aeolian activity. In 1973 Soviet Mars 5 and 6 revealed more data on the
surface and the atmosphere, followed by the Viking missions in 1975 (see next chapter).

The first completely successful mission after the Viking Missions the Mars Pathfinder Mission, was launched in
1997. Apart from the collection of many atmospheric data, such as early morning water ice clouds, the focus
was on surface science by using a small rover to drive around the surface [4]. After Pathfinder only two orbiter
reached Mars - Mars Global Surveyor (MGS), launched in 1996, and Mars Odyssey in 2001. MGS discovered
possibly water on Mars, by imaging relatively young...
landforms and gullies. These results were endorsed by the results of the Mars Odyssey that found large quantities of hydrogen and water-ice just underneath the surface of Mars [5] [6] [7]. The results of these missions have put the search for possible life in a completely new perspective.

2. THE VIKING MISSION

The Viking mission consisted of two spacecraft, Viking 1 and Viking 2, each composed of an orbiter and a lander [8]. The main goals of the mission were to obtain high resolution images of the Martian surface, characterise the structure and composition of the atmosphere and surface, and search for evidence of life. The Viking landers carried several experiments, among them a biological and a molecular analysis experiment, who's purpose was the search for life related organic molecules and organisms.

- Biological experiments and results
The biology experiment searched for the presence of Martian organisms by looking for metabolic products. The experiment was equipped with three instruments that incubated samples of the Martian surface under varying environmental conditions, the gas exchange (GEx) experiment, the pyrolytic release (PR) or carbon assimilation experiment and the labelled release (LR) experiment [9] [10].

The GEx experiment measured in two modes the production and/or uptake of CO₂, N₂, CH₄, H₂, and O₂ [11]. In the "humid" mode, a nutrient medium, composed of a complex mixture of organic compounds and inorganic salts, was added without soil contact, and the soil was only exposed to the water vapour in the atmosphere. The results showed that some CO₂ and N₂ was desorbed from the soil and that the oxygen accumulated rapidly after humidification in the headspace above the sample. This rapid accumulation of oxygen, in combination with the facts that (a) adding water in a later stadium had not caused further release of oxygen, and (b) oxygen was released from a sterilised sample (145° C for 3.5 hours), clearly excludes a biological explanation of the results. The results from the "wet" mode confirmed this interpretation [7], because (a) the absorption of CO₂ also occurred in sterile samples, and (b) because the CO₂ production rate slowed down, when the used nutrient was replaced with fresh nutrient.

The PR experiment was designed to detect the photosynthetic or chemical fixation of ¹⁴CO₂ or ¹²CO or both [12]. The results showed that heating the samples to 175°C strongly reduced the reaction of ¹⁴CO and ¹⁴CO₂ in the sample, although heating to 90°C did not have any effect. The data also suggested that reaction proceeded better in light, but storage of the soil within the spacecraft (in the dark) for four months did not affect the reaction.

The LR experiment used radio-respirometry to detect metabolic processes [13] [14]. The LR showed the rapid release of the labelled gas when a aqueous solution of dilute radioactive organic compounds was added. After the initial reactions the evolution of labelled gas slowly continued and terminated when 90% of the nutrients were still left. When the samples were heated to low temperatures (40-50°C) the reaction slowed down, raising the temperature to 160°C caused the reaction to end. The reactions in the soil had stopped as well when the samples were stored at spacecraft temperature for four months.

- Molecular analysis experiments and results
The main purpose of the molecular analysis experiments of the Viking landers was to investigate whether or not there are organic compounds present at a significant concentration at the surface of Mars [6]. A gas chromatograph mass spectrometer (GCMS) was used to analyse the soil. In the four samples taken from surface and subsurface material from both landing sites, no organic compounds of Martian origin were present at levels in the parts per billion (ppb) and parts per million (ppm) range [6]. Furthermore no traces of organic substances expected from meteoritic delivery were found [15].

- Conclusions
The results of the molecular analysis experiments unanimously point towards the absence of organic compounds in the Martian soil. Several explanations have been proposed, which all point towards the suggestion that the production and infall rate of organic material is much smaller then the destruction rate. The biology experiments initially could have pointed to life in the Martian soil, especially the data of the LR experiments. However, in combination, and considering the non-detection of any organic compound in the upper soil made people search for a non-biological explanation. Recent experiments indicate that the pyrolysis products generated from several million bacterial cells per gram of Martian soil would not have been detected at the ppb level, by the molecular analysis experiment [16].

3. POSSIBLE DESTRUCTION MECHANISMS

Since the science results of the Viking mission several scenarios have been proposed to explain the absence of organic material in the Martian regolith. A combination of (a) short wavelength UV, which destroys organic compounds, and (b) oxygen, H₂O₂, metaloxides, or other oxidising agents is able to remove organic
compounds from the surface [6]. Additional support for this theory comes from recent work that showed that H₂O₂ is a good candidate for the thermally labile oxidant that produced rapid evolution of [HCO₂] during the Viking LR experiments [17]. Furthermore, new evidence for the reactivity of the Martian soil due to superoxide ions, such as O₂⁻, has been published [18].

Overall the hypothesis involving oxidising agents in the regolith is still the most widely accepted one, although this subject requires future investigations.

4. THE MARS SIMULATION CHAMBER

It is still unclear why no traces of organic compounds, which should have been accumulated from meteoritic delivery [19], have been found by Viking in the Martian surface. Likely organic compounds are destroyed on the exposed surface, but may survive when protected in greater depth of Martian dust or inside rocks. In order to determine the stability of specific organic compounds, laboratory simulations are essential to understand chemical pathways on the Martian surface.

In this context an experimental programme is developed at the European Space Research and Technology Centre of ESA (ESTEC) and at Leiden University. The experimental research will include the investigation of organic molecules subjected to simulated Martian atmospheres and soil analogues. An atmospheric simulation chamber in combination with a solar simulator will be used to collect data on the combined effects of UV photo processing, atmospheric conditions and the presence/absence of oxidizing agents on organic molecules. All those described effects will be studied independently and in combination in order to get insight in the individual processes and their interactions on organics in the Martian soil. The organic compounds represent analogues for abundant meteoritic and cometary molecules and entail aliphatic and aromatic hydrocarbons, fullerenes, amino acids and nucleo-bases, carbonaceous solids and terrestrial analogues (i.e. kerogens).

The Mars Simulation Chamber (MSC) (Fig. 1 and 2), used for the experiments, is a 80 cm long, 60 cm high vacuum chamber, which will be filled with a simulated Mars atmosphere. This atmosphere can be adjusted to present and hypothetical past Martian conditions. To allow sample handling without external contamination two differentially pumped rubber gloves, similar to a glove box, were mounted on the side of the chamber. The solar simulator is mounted on top of the chamber to provide past and current solar spectra on Mars.

![Figure 1. Mars Simulation Chamber](image)

![Figure 2. Schematic outline of simulation chamber](image)

Six, 20 cm long, 1.5 cm diameter, stainless steel, sample holders (Fig. 3 and 4) will be filled with a mixture of Martian soil analogues and organic samples and sealed with O-ring stoppers. The sample holders will be mounted onto a copper ground-plate that allows temperature control by means of slush solutions that are pumped through the plate and stored in the MSC.

![Figure 3. Sample holder](image)

Three sample sites allow in-situ measurements of the volatiles at three different heights within the containers. The temperature of the medium in the chamber can be cooled by means of a cold shroud positioned around the
sample containers. The temperature of the sample holders can be set within the same range. Feed-through lines allow the cooling medium to enter the cold-shroud and the sample holders.

The experimental protocol comprises three parts: preparation of the chamber, setting of the experimental parameters, and in situ and post-processing measurements of the samples.

SUMMARY

Experiments will be performed using a vacuum chamber. In this chamber the Martian atmosphere, atmospheric pressure and temperature can be simulated, as well as the solar spectrum. These parameters can be adapted to the present and the past situation on Mars.

The following effects will be studied by the experiments:
* The effects of the Martian atmosphere.
* The effect of UV irradiation on organic molecules embedded in the soil.
* The effect of oxidation on organic molecules in the soil.
* The effect of thermal cycling on the surface.

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REFERENCES


