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Investigating complex organic compounds in a simulated Mars environment

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Abstract: The search for organic molecules and traces of life on Mars has been a major topic in planetary science for several decades. 26 years ago Viking, a mission dedicated to the search for life on Mars, detected no traces of life. The search for extinct or extant life on Mars is the future perspective of several missions to the red planet, for example Beagle 2, the lander of the Mars Express mission. In order to determine what those missions should be looking for, laboratory experiments under simulated Mars conditions are crucial. This review paper describes ongoing experiments that are being performed in support of future Mars spacecraft missions. Besides the description of the experiments, the experimental hardware and set-up, this paper also gives the scientific rationale behind those experiments. The historical background of the search for life on Mars is outlined, followed by a description of the Viking Lander *biology* and *molecular analysis experiments* and their results, as well as a summary of possible reasons why no organic compounds have been detected. A section concerning organic compounds in space and related experiments discusses the organic molecules we will use in simulation experiments. The set-up is discussed briefly in the following section. We conclude with an overview of future missions, stressing the relation between these missions and our laboratory experiments. The research described in this article has been developed as part of a Mars Express Recognized Cooperating Laboratory (RCL), and for planned future Mars missions such as the PASTEUR lander.

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Mars, the historical perspective

For centuries humankind has been curiously watching the night sky with its stars and planets. One of the fundamental questions has always been whether there is life beyond the Earth. Mars, the next planet further out in the solar system has always played a major role in this context (see Fig. 1).

In 1892 Camille Flammarion published a book called *La Planète Mars et ses Conditions d'Habitabilité*. It contained a compilation of all credible telescope observations of Mars carried out until then, and Flammarion's main conclusion was that Mars has dry plains and shallow seas, and that it was obviously habitable. He also speculated about canals built by a higher civilization than the one on Earth. This speculation was probably built on the apparent 'discovery' of canals by Giovanni Schiaparelli in 1877, who thought that he saw a geometric network of straight canals appearing in pairs. When Percival Lowell heard about the canals on Mars he got so excited that he immediately started to build his own observatory. Even before he started his observations, he stated that the canals could be nothing other than the result of the work of very intelligent beings. His observations showed that the canal network was too regular to be natural, so he concluded that they should have been created by a species more advanced than humans. Furthermore, he published that the polar caps seen on the planet could be nothing other than water-ice and that the dark spots seen along the canals were growth of vegetation. His theories were widely accepted until Lowell started writing about similar canals on Venus, which were very soon afterwards proven not to exist. Very recently, Sheehan & Dobbins (2002) published that Lowell narrowed the lens of his telescope so far that he created an ophthalmoscope, with which he saw the reflection of his own eyeball. Nevertheless, several of his Martian theories lasted for decades.

Even in 1961, only a few years before the first space mission was launched to Mars, Vaucouleurs still published some of Lowell's ideas, in his *The Physics of the Planet Mars*, Vaucouleurs wrote that Mars had an 85 mbar nitrogen atmosphere, was cold, but with a tolerable surface temperature, had

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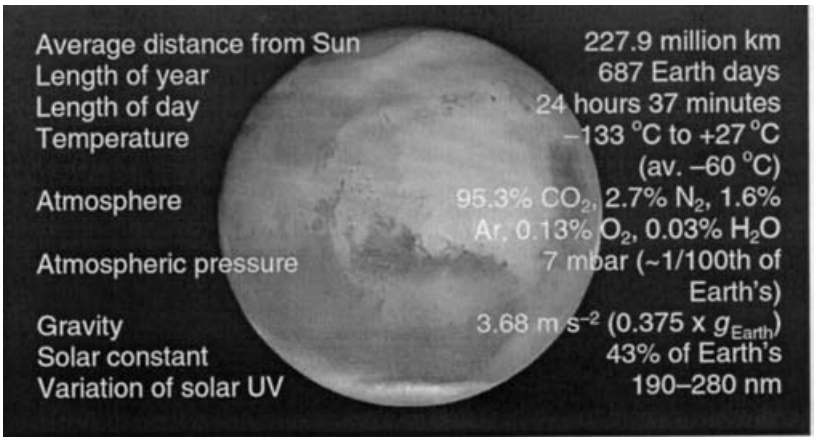

Fig. 1. Mars, picture courtesy: NASA.

seasonal changes probably owing to vegetation and that the polar ice caps were not composed of frozen CO_2 but of water-ice.

Mars during the space age

In 1960 the Soviet Union started a new era in the exploration of Mars, by sending a spacecraft, Mars 1960A, to Mars. Unfortunately, this mission and seven of its successors failed, making US Mariner 4 in 1965 the first mission to reach Mars. Mariner 4, looking at Mars from a distance of 9846 km, sent back data suggesting that Mars looked similar to the Moon, with a cratered surface (Chapman *et al.* 1969). Also a surface atmospheric pressure of 4.1–7.0 mbar could be estimated and no magnetic field was detected. Mariner 6 and 7, launched in 1969, did more detailed research and revealed that the surface of Mars is very different from the surface of the Moon, in contrast to the results of Mariner 4. Furthermore, the spacecraft showed a south polar cap predominantly composed of CO_2 and an atmospheric surface pressure of between 6 and 7 mbar (e.g. Herr *et al.* 1970). In 1971 the Soviet Union sent two spacecraft to Mars, Mars 2 and 3. In spite of the failing of the landers, 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 (e.g. Marov & Petrov 1973). The data led to the following discoveries:

- mountains up to 22 km;
- H_2O in the upper atmosphere;
- surface temperatures of 163–286 K;
- surface pressures of 5.5–6 mbar;
- water vapour concentrations 5000 times less than in Earth's atmosphere;
- the base of the ionosphere starting at 80–110 km altitude; and
- grains from dust storms as high as 7 km in the atmosphere.

The first detailed images of the volcanoes, Vales Marineris, the polar caps and the moons Phobos and Deimos, were delivered by Mariner 9 (e.g. Veverka *et al.* 1974). This spacecraft, launched in 1971, also revealed new data on global dust storms, the tri-axial figure of Mars, the rugged gravity field and evidence for surface Aeolian activity. In 1973 two partly successful Soviet missions were launched, Mars 5 and 6, which revealed more data on the surface and the atmosphere, followed by the Viking missions in 1975 (see the next section). After more than a decade two Phobos missions were launched by the Soviet Union in 1988. Unfortunately, both missions failed due to communication problems, one after 2 months and one after 9 months.

The next completely successful mission to the red planet, the Mars Pathfinder Mission, was launched in 1997, and landed in the Ares Vallis region at 19.33° N, 33.55° W. Using a small rover to drive around on the surface much atmospheric and surface data was obtained (e.g. Golombek 1997). Some rocks at the landing site appeared to be high in silica, unlike that which was expected from the Martian meteorites found on Earth. Rounded pebbles and grooved rocks suggested liquid water in the past. The elemental composition of the soil appeared to be similar to the landing sites of Viking 1 and 2. Whirlwinds that probably mix dust into the atmosphere and cause the so-called gardening of the soil, were analysed. Early morning water-ice clouds, which evaporated when the temperature rose, were detected in the lower atmosphere, as well as abrupt temperature fluctuations.

After Pathfinder six missions were launched of which the Japanese Nozomi-planetB mission is still on its way and will arrive in 2003. The only two missions that succeeded in reaching Mars were Mars Global Surveyor (MGS), launched in 1996, and 2001 Mars Odyssey. MGS showed the possible presence of water on Mars by imaging relatively young landforms and gullies. This spectacular result was endorsed by the results of the Mars Odyssey mission which found large quantities of hydrogen that is assumed to be water-ice just underneath the surface of Mars (Boynton *et al.* 2002; Feldman *et al.* 2002; Mitrofanov *et al.* 2002). The results of these missions have put the search for possible life in a completely new perspective.

The Viking mission

The Viking mission consisted of two spacecraft, Viking 1 and Viking 2, each composed of an orbiter and a lander (Soffen

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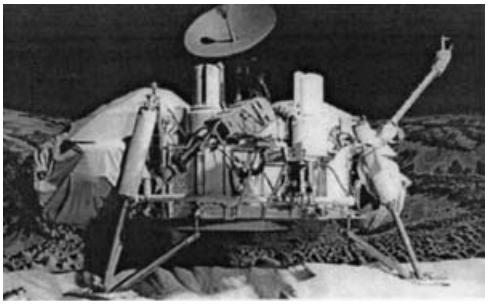

Fig. 2. Viking lander (picture courtesy NASA).

1977). The main goals of the mission were to obtain high-resolution images of the Martian surface, to characterize the structure and composition of the atmosphere and surface, and to search for evidence of life. Viking 1 was launched on August 20, 1975 and entered Mars orbit on June 19, 1976. The first month of orbit was used to find appropriate landing sites for the Viking Landers. On July 20, 1976 the Viking 1 Lander landed at Chryse Planitia (22.48° N, 49.97° W). Viking 2 was launched September 9, 1975 and arrived at Mars on August 7, 1976. The Viking 2 Lander landed at Utopia Planitia (47.97° N, 225.74° W) on September 3, 1976.

Lander experiments

The Viking landers (Fig. 2) carried several experiments onboard, among them a biological and a molecular analysis experiment. These experiments had as their main purpose the search for life related organic molecules and organisms.

Biological investigations and results

The *biology experiment* searched for the presence of Martian organisms by looking for metabolic products. To perform this search 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 (Biemann *et al.* 1977; Klein 1978).

The *GEx experiment* measured the production of CO_2, N_2, CH_4, H_2 and O_2, and the uptake of CO_2 by soil samples (Oyama & Berdahl 1977). A sample was sealed and purged with He, followed by incubation with a mixture of He, Kr and CO_2. Thereafter a nutrient solution was added and the sample was incubated. At intervals, samples of the atmosphere were taken and analysed by a gas chromatograph with a thermal conductivity detector. The experiments were performed in two modes: the 'humid' and the 'wet' mode.

In the 'humid' mode the nutrient medium, composed of a 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 CO_2 and N_2 were released from the soil and that oxygen was produced rapidly after humidification. This rapid production of oxygen, in combination with the facts that (a) adding water in a later stage did not cause further release of oxygen and (b) oxygen was also released from a sterilized sample (145 °C for 3.5 h), clearly excludes a biological explanation of the results.

In the 'wet' mode the nutrient made contact with the soil. The results from the 'wet' mode confirmed results of the 'humid' mode (Klein 1978), because (a) the release of CO_2 also occurred in sterile samples and (b) because the CO_2 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 $^{14}CO_2$ or ^{14}CO or both (Horowitz *et al.* 1977). Soil samples were incubated in the presence of an atmosphere of ^{14}CO or $^{14}CO_2$, some with and some without simulated sunlight. After several days of incubation each sample was heated to 120 °C to remove the ^{14}CO and $^{14}CO_2$ that had not reacted. Next, the soil was pyrolized at 650 °C and organic products were collected in an organic vapour trap. Finally, the trap was heated to combust any organic material to CO_2 and any evolved radioactive gas was measured. The results showed that heating the samples at 175 °C strongly reduced the reaction of ^{14}CO and $^{14}CO_2$ with the sample, although heating to 90 °C did not have any effect. The data suggested that the reaction proceeded better in light, but storage of the soil within the spacecraft (in the dark) for 4 months did not affect the reaction.

The *LR experiment* used radio-respirometry to detect metabolic processes (Levin & Straat 1977, 1981). This was done by adding an aqueous nutrient solution labelled with radioactive carbon (^{14}C) to the soil sample. The atmosphere over the samples was continuously monitored to detect any radioactive gases released from these non-volatile nutrients. The LR produced the most controversial results. The results showed the rapid release of labelled gas upon addition of the nutrients. After an initial high peak, the gas production quickly dropped to a level where no further gas production could be detected. At that point 90% of the nutrients were still left. When the samples were heated to moderate temperatures (40–50 °C) the reaction slowed down, whereas raising the temperature to 160 °C caused the reaction to end. The reactions in the soil also stopped when the samples were stored at the spacecraft for 4 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 (Biemann *et al.* 1977). The soil analyses were performed using a gas-chromatograph mass-spectrometer (GCMS) with a high sensitivity, high structural specificity and broad applicability to a wide range of compounds. A stepwise heating process vaporized substances from the surface material. Using $^{13}CO_2$ the released volatiles were then brought towards the Tenax gas-chromatographic (GC) column, where, using hydrogen as a carrier gas, the substances were separated. After hydrogen was removed, the residual stream moved into the mass spectrometer (MS), which created a mass spectrum (masses from 12 to 200 amu) every 10 s for the 84 min of the gas chromatogram. For

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atmospheric measurements, gases were directly introduced into the MS, bypassing the GC column.

In the four samples taken from surface and subsurface material from both landing sites, no organic compounds, of Martian origin, containing more than two carbons, were present at levels in the parts per billion (ppb) range and no one- and two-carbon-containing compounds at the parts per million (ppm) level (Biemann *et al.* 1977). Furthermore, no traces of meteoritic material were found (Biemann & Lavoie 1979).

Conclusions from the Viking experiments

The results of the molecular analysis experiments clearly 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 are much smaller than the destruction rate.

The biology experiments initially could have pointed to life in the Martian soil, especially the data from 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. Based on these results the presence of a destructive oxidizing agent, such as metalperoxide or a superoxide, in the soil is suggested.

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 (Glavin *et al.* 2001). This has already been suggested by Klein (1978, 1979), but it was never confirmed with experimental data. Other research concluded that organic molecules, such as benzenecarboxylates, oxalates and perhaps acetates are likely to have been formed on the Martian surface via oxidation of delivered organic material (Benner *et al.* 2000). These compounds were very difficult for Viking to detect.

Origin of organic compounds on Mars

The early Earth and Mars may have been seeded with organic material from meteorites and comets that had survived impact. Such molecules may have been destroyed, altered or displaced into deeper soil layers, where they are protected from radiation and oxidation. The continuous, planet-wide meteoritic mass influx on Mars is estimated at between 2700 and 59 000 t yr^{-1}. This is equivalent to a meteoritic mass accretion rate of between 1.8×10^{-5} and 4×10^{-4} g m^{-2} yr^{-1} (Flynn & McKay 1990).

Organic matter in asteroids, comets and planetary satellites

Evidence for solid organic material on the surfaces of solar system bodies comes from astronomical and spacecraft observations. Three main groups of objects are important in this context: low-albedo asteroids, which populate mainly the outer part of the asteroid belt, comets and planetary satellites with low-albedo surface features. The cause of the low albedos for these objects is believed to be the presence of macromolecular carbon-bearing molecules (kerogen-like material), elemental carbon and other opaque minerals (e.g. magnetite).

Low-albedo asteroids are thought to be the main source of most carbonaceous chondrites. They have largely featureless spectra, and their albedos are similar to the C-bearing dark carbonaceous chondrites. Thus, C- and also P- and D-type asteroids are thought to contain organic carbon and/or complex organic compounds in their regolith (Cronin *et al.* 1988). Comparisons of telescopic reflectance spectra of C- and G-type asteroids with laboratory reflectance spectra of carbonaceous meteorites show a close match when the Murchison samples were heated to 900 °C (Hiroi *et al.* 1993). A spectroscopic survey of primitive objects in the solar system and a comparison of these spectra to laboratory samples that included meteorite powder, tar sand, carbon lampblack, coal and synthetic graphite provided an upper limit of 3% organic carbon on the surfaces of main belt asteroids (Luu *et al.* 1994). Comets are thought to contain significant amounts of organic compounds (Kissel & Krueger 1987). Estimates are in the range of 23 wt% for the complex organic refractory material and 9 wt% for the extremely small carbonaceous particles (Greenberg 1998).

Fig. 3 shows that the relative amino acid composition in the Martian meteorites is close to identical to the terrestrial samples, and that these two sample sets differ significantly from the amino acid composition of the carbonaceous chondrites. Note that the AIB/Gly ratios for Renazzo, Allende, Martian meteorites, Tagish Lake, as well as all terrestrial samples are upper limits owing to the non-detection of AIB in these samples. Also, the D-Ala/Gly ratios in Renazzo and Allende as well as the β-Ala/Gly in all Martian meteorites are upper limits.

A recently discovered class of solar system bodies is the Centaurs, small bodies with orbits crossing those of the outer planets (Yeomans 2000). In contrast to the featureless reflectance spectra of low-albedo asteroids in the main belt, one object in this class, 5145 Pholus, shows a unique absorption pattern in its reflectance spectrum that can be explained by the presence of a common silicate (olivine), a refractory solid complex of organic molecules (tholin), water and methanol ices, and carbon in the form of partially processed remnants of the original interstellar organic material on its surface (Cruikshank *et al.* 1998). The spectrum is so well fitted by a rigorous model that includes all of the basic components of comets that it seems reasonable to assume that Pholus is the nucleus of an inactive comet.

Titan, the largest moon of Saturn, has a thick atmosphere with a surface pressure of 1.5 bar and an average surface temperature of 95 K. An orange-coloured haze of aerosol particles prevents a direct view on to the surface. Laboratory experiments have shown that this haze is spectroscopically similar to the mixture of organic material, known as 'tholin', which has been produced by photochemical experiments in the laboratory (McDonald *et al.* 1994). Tholins yield amino acids upon acid hydrolysis, indicating the possibility of aqueous organic chemistry on Titan if liquid water is present for

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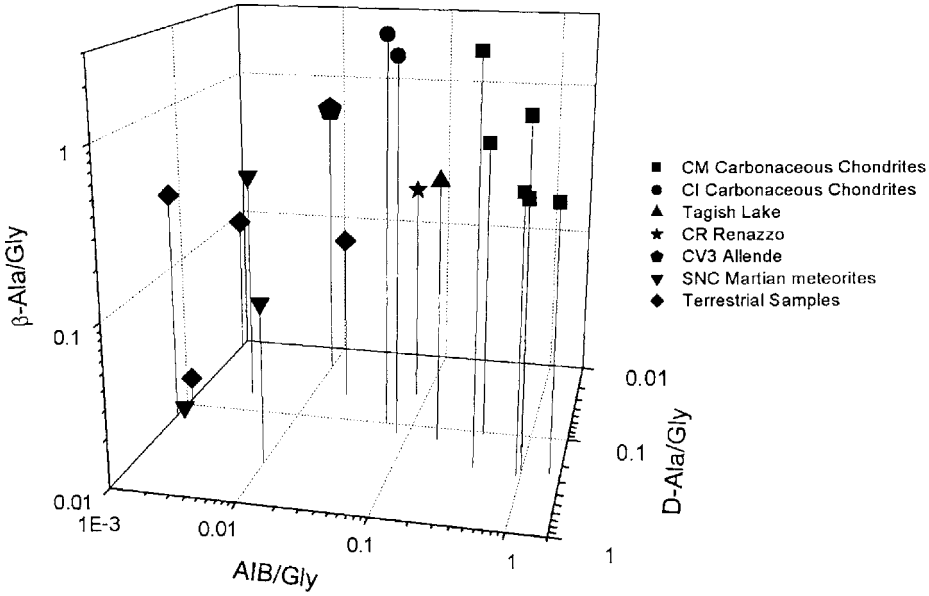

Fig. 3. The relative amino acid composition in the Martian meteorites is close to identical to the terrestrial samples, and that these two sample sets differ significantly from the amino acid composition of the carbonaceous chondrites. Note that the AIB/Gly ratios for Renazzo, Allende, Martian meteorites, Tagish Lake, as well as all terrestrial samples are upper limits due to the non-detection of AIB in these samples. Also, the D-Ala/Gly ratios in Renazzo and Allende as well as the β-Ala/Gly in all Martian meteorites are upper limits.

significant periods of time. In addition, because of its large inventory of organic compounds, including hydrocarbons and nitriles, detected in its atmosphere, Titan is considered a natural laboratory for prebiotic organic chemistry, with the main difference with the early Earth being mainly the average surface temperature over time (Sagan *et al.* 1992).

Meteorites

Laboratory evidence for the presence of organic compounds on other solar system bodies comes primarily from the research on carbonaceous chondrites, which are the most primitive meteorites in terms of their elemental composition. These meteorites contain up to 3 wt% of organic carbon, the majority of which is bound in an insoluble component. The soluble fraction can be obtained by treating a crushed meteorite sample with a series of solvents of different polarity, which leads to the presence of complex mixtures of compounds in the individual extracts. The total soluble fraction of CI(1) and CM(2) chondrites was estimated to contain 30–40% of the total carbon (Hayes 1967), which is probably an upper limit owing to the additional dissolution of inorganic salts in the polar solvents (Cronin & Chang 1993).

The insoluble fraction of carbonaceous chondrites is composed of macromolecular matter that is commonly referred to as 'kerogen-like' material (Gardinier *et al.* 2000). Kerogen is insoluble macromolecular organic matter, operationally defined as the organic residue left after acid demineralization of a rock. The study of organic compounds in this phase is similar to their analysis in coal, oil shale and petroleum source rocks and involves the dissolution of the mineral fraction of the rock by attack with HCl in combination with HF (Robl & Davis 1993). The structure of the macromolecular carbon, the 'polymer-like' component in the insoluble carbon fraction, is not well characterized. Based on pyrolytic release studies, Zinner (1988) calculated a formula of $C_{100}H_{48}N_{1.8}O_{12}S_2$ for this material in Murchison. Results from ^{13}C nuclear magnetic resonance spectroscopic measurements of partially demineralized samples also suggest that polycyclic aromatic rings are an important structural feature in the insoluble carbon of the Murchison, Orgueil and Allende meteorites (Cronin *et al.* 1987). However, these measurements also suggest that this material contains abundant aliphatic substituents that are probably bridging the aromatic units. All of these features point to a resemblance of the meteoritic macromolecular carbon to aromatic terrestrial kerogens.

The soluble fraction of the organic matter in carbonaceous chondrites can be obtained by extracting powdered meteorite samples with solvents of varying polarity. About one-third of this soluble fraction is comprised of polycyclic aromatic hydrocarbons (PAHs), with carboxylic acids and fullerenes present at abundances of one order of magnitude less. All other compound classes, including the biologically relevant amino acids and nucleobases, are present in concentrations of 1–100 ppm (see Table 1).

More than 70 extraterrestrial amino acids and several other classes of compounds including carboxylic acids, hydroxycarboxylic acids, sulphonic and phosphonic acids, aliphatic, aromatic and polar hydrocarbons, fullerenes, heterocycles as well as carbonyl compounds, alcohols, amines and amides have been detected in the CM meteorite Murchison as well as in other carbonaceous chondrites (see Table 1). Several amino acids that are extremely rare on Earth, such as α-aminoisbutyric acid (AIB) and isovaline, were found to be among the most abundant amino acids in several CM-type

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Table 1. *Abundances of water-soluble organic compounds found in meteorites* (*Botta & Bada 2002*). *Amino acids concentrations have been determined for several CI and CM chondrites. All other data are for the CM chondrite Murchison* (*except the aromatic hydrocarbons and the fullerenes*)

Compound class	Concentration (ppm)
Amino acids	
CM meteorites	17–60
CI meteorites	~5[a]
Aliphatic hydrocarbons	>35
Aromatic hydrocarbons	3319[b]
Fullerenes	>100[c]
Carboxylic acids	>300
Hydroxycarboxylic acids	15
Dicarboxylic acids and hydroxydicarboxylic acids	14
Purines and pyrimidines	1.3
Basic N-heterocycles	7
Amines	8
Amides linear	>70
Cyclic	>2[d]
Alcohols	11
Aldehydes and ketones	27
Sulphonic acids	68
Phosphonic acids	2

[a] Average of the abundances in the CI carbonaceous chondrites Orgueil and Ivuna (Ehrenfreund *et al.* 2001).
[b] For the Yamato-791198 carbonaceous chondrite (Naraoka *et al.* 1988).
[c] 0.1 ppm estimated for C_{60} in Allende (Becker *et al.* 1994).
[d] Cooper & Cronin (1995).

carbonaceous chondrites (Botta *et al.* 2002). In contrast, the CI carbonaceous chondrites Orgueil and Ivuna showed only high abundances of glycine and β-alanine. Only very low abundances of AIB, isovaline and other more complex amino acids were detected, which indicates that these meteorites originated on a parent body with an entirely different chemical composition or a different thermal evolution (Ehrenfreund *et al.* 2001). In all organisms on Earth, only the L-enantiomers (left-handed forms) of chiral amino acids are incorporated into proteins and enzymes. In contrast, the a-biological synthesis of chiral amino acids always yields a 1:1 mixture of the D- and L-enantiomers (a *racemic* mixture). Therefore, the molecular architecture of these compounds provides a powerful tool for discriminating between biological and non-biological origins of amino acids in meteorites. Until recently, all chiral amino acids (e.g. alanine or isovaline) in meteorite extracts were found to be present as *racemic* mixtures, which indicates an abiotic origin and therefore the presence of indigenous extraterrestrial amino acids. Enantiomeric excesses (EEs) of the L-enantiomer of the two diastereoisomers of 2-amino-2,3-dimethylpentanoic acid (DL-α-methylisoleucine and DL-α-methylalloisoleucine) as well as isovaline, which are non-biological amino acids that, owing to their molecular architecture, are not prone to racemization (the conversion of an enantiomerically pure compound into a racemic mixture), were found in Murchison hot-water extracts (Cronin & Pizzarello 1997).

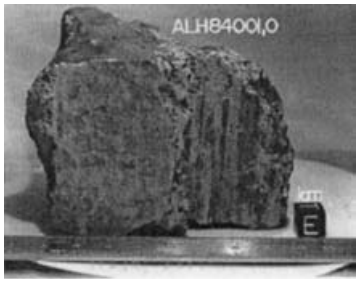

Fig. 4. ALH 84001, picture courtesy NASA.

The content of N-heterocyclic compounds in meteorites was investigated by Schwartz and co-workers about 25 years ago. They found the pyrimidine uracil, a monocyclic aromatic ring containing two nitrogen atoms, in the Murchison, Murray and Orgueil meteorites in concentrations of between 37 and 73 ppb (Stoks & Schwartz 1979). Later, the purines adenine, guanine, xanthine and hypoxanthine, which are bicyclic rings with four nitrogen atoms and slightly different substitution pattern, were found in the same meteorites at abundances of between 542 and 1649 ppb (Stoks & Schwartz 1981). Finally, several other N-heterocyclic compounds, including 2,4,6-trimethylpyridine, quinoline, isoquinoline, 2-methylquinoline and 4-methylquinoline, were positively identified in the formic acid extract of the Murchison meteorite (Stoks & Schwartz 1982). Higher derivatives of quinolines and isoquinolines have also been detected in this meteorite (Krishnamurthy *et al.* 1992).

Generally, meteoritic organic matter is enriched in deuterium, and distinct groups of organic compounds show isotopic enrichments of carbon and nitrogen relative to terrestrial matter (Irvine 1998). These enriched isotope values, especially for deuterium, can be traced back to the isotopic fractionation associated with the very low temperatures in the interstellar medium, where the precursors (e.g. HCN, NH_3 and carbonyl compounds for the amino acids) formed by gas-phase ion–molecule reactions and reactions on interstellar grain surfaces (for reviews see Smith 1992; Herbst 1995).

ALH84001

In 1996 it was reported that the Martian meteorite ALH84001 contained possible evidence for life on Mars (see Fig. 4). It has been argued that this meteorite showed biogenic fossils (McKay *et al.* 1996). The PAH component of meteorites has been invoked, as an integral part of the claim that the Martian meteorite ALH84001 contains extinct microbial life, a claim that is currently the subject of intense debate (e.g. Jull *et al.* 1998). Examination of carbonate globules and bulk matrix material of ALH84001 using laser absorption mass spectrometry indicated the presence of a high molecular weight organic component which appears to be extraterrestrial in origin (Becker *et al.* 1999).

Later research by Barrat *et al.* (1999) on the Tatahouine meteorite, a non-Martian meteorite that fell in 1931 in Tunisia, showed similar features to those found in ALH84001, which were definitely formed on Earth. Kirkland *et al.* (1999) demonstrated that the bacteria-shaped objects seen in ALH84001

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can be formed without any biology being involved. This conclusion was also drawn by Golden *et al.* (2000), who published that 'carbonates with chemical zoning, composition, size and appearance similar to those in ALH84001 can be achieved by purely inorganic means and at a relatively low temperature'. Also Zolotov & Shock (2000) arrived at a similar conclusion, that, based on thermochemical calculations, the PAHs in ALH84001 (and the proportions of the various PAH species) could reasonably have been produced inorganically, without biological influences.

Thomas-Keprta *et al.* (2001, 2002) continued the research started by McKay *et al.* (1996) on carbonate globules and characterized a subpopulation of magnetite (Fe_3O_4) crystals, which were found chemically and physically identical to terrestrial, magnetites produced by the magnetotactic bacteria strain MV-1. The crystals are both single-domain, chemically pure and have both a crystal structure called truncated hexa-octahedral, which on Earth are exclusively produced biogenically. They suggested that the magnetite crystals were probably produced by a biogenic process and thus interpreted these results as evidence of life. Further research implied that approximately 25% of the magnetite crystals embedded in ALH84001 were identical to terrestrial biogenic magnetite.

Possible destruction mechanisms on the Martian surface

Since the science results of the Viking mission several scenarios have been proposed to explain the absence of organic matter in the Martian soil. Biemann *et al.* (1977) suggested that the organic compounds would be destroyed by a combination of short-wavelength ultraviolet (UV) radiation and oxygen, H_2O_2, metaloxides or other oxidizing agents. These oxidizing agents cause organics in combination with short-wavelength UV to be removed much faster than by UV alone and are even destructive in the dark. The oxidizing agent hypothesis is the most important one, although there are also arguments against it. The major reasons for this hypothesis are described below (see also Bullock *et al.* 1994).

(a) In the Viking experiments (see Section 3.1) the soil released O_2 when humidified in GEx (Oyama & Berdahl 1977, 1979), but when the samples were wetted with nutrient solution no additional O_2 was released. On the other hand, during wetting a slow evolution of CO_2 occurred, indicating oxidation of organics by an oxidizing agent. When the samples were heated to 145 °C the amount of O_2 was reduced by 50% but not eliminated.
(b) The GCMS in the molecular analysis experiment did not detect organics in surface and below-surface samples, although there are at least two mechanisms that could produce organics, meteoritic infall, estimated by Flynn & McKay (1990) and UV production (Biemann *et al.* 1977).
(c) The LR experiment showed a rapid release of $^{14}CO_2$ when samples were wetted with an aqueous nutrient medium containing ^{14}C. This rapid release was completely removed by heating at 160 °C for 3 h and partially destroyed when heated at 40–60 °C. The sample stayed unaffected by storage at 18 °C for short time, but was lost after 2–4 months at that temperature.

Bullock *et al.* (1994) proposed that H_2O_2 is a good candidate for the thermally labile oxidant that produced rapid evolution of $^{14}CO_2$. This assumption is based on the results of the Viking LR experiments and experiments performed after Viking. Hunten (1979) suggested that H_2O_2, which could be the source of the oxidants in the LR experiments, is produced in the atmosphere by photochemical reaction at a rate of 2×10^9 molecules $cm^{-2}\,s^{-1}$. Huguenin *et al.* (1979) and Huguenin (1982) have suggested that chemisorbed H_2O_2 is produced by frost weathering of olivine. In the same year Oyama & Berdahl (1979) reproduced the LR experiment by reacting formate with H_2O_2 and γ-Fe_2O_3 mixed with Martian surface minerals. They also duplicated the slow CO_2 production in the LR and GEx experiments with a mixture of γ-Fe_2O_3 and formate. These findings were endorsed by Ponnamperuma *et al.* (1977), who found $^{14}CO_2$ production when the Viking nutrient mixture was added to γ-Fe_2O_3, as well.

However, there are also arguments against H_2O_2. Levin & Straat (1981) published that: (1) H_2O_2 reacted also with other compounds in nutrients than formate, meaning that the H_2O_2 hypothesis did not account for the fact that only one compound in LR was oxidized to CO_2 and (2) H_2O_2 is much more thermally labile than oxidant in an LR nutrient. Other arguments against the H_2O_2 hypothesis are the short lifetime of only 10^4 s against UV destruction on the Martian surface and that H_2O_2 alone cannot explain the thermally stable GEx results.

Another explanation in the oxidant hypothesis was given by Yen *et al.* (2000), who proposed 'that superoxide radical ions (O_2^-) are responsible for the chemical reactivity of the Martian soil'. This was concluded from laboratory experiments on the formation of O_2^- on Mars, which they expect to form readily on mineral grains at the surface. Addition of water to O_2^- produces O_2, HO_2^- and OH^-. This explains the release of O_2 during humidification and injection of water into the Martian soil samples by Viking, and is consistent with the decomposition of organic nutrients in the Viking experiments. The absence of organic compounds can also be explained by the presence of O_2^-, and is probably caused by decomposition of oxygen radicals and by the products of O_2^- reactions with the atmospheric water vapour.

A substantial fraction of $\sim$120 molecules that have been identified in interstellar and circumstellar regions are organic in nature (Ehrenfreund & Charnley 2000). Large carbon-bearing molecules (such as polycyclic aromatic hydrocarbons, fullerenes and unsaturated chains) are also thought to be present in the interstellar medium. The presence of large aromatic structures is demonstrated by infrared observations of the interstellar medium in our galaxy and in extragalactic environments (Tielens *et al.* 1999). A variety of complex aromatic networks are likely to be present on carbonaceous grains (see Henning & Salama 1998 for a review).

The total annual influx of organic material from space (interplanetary dust particles (IDPs), meteorites, etc.) on Mars is estimated at approximately 300 t yr^{-1} (Chyba & Sagan 1992). This influx will most likely consist of the above-mentioned large aromatic networks, PAHs, fullerenes,

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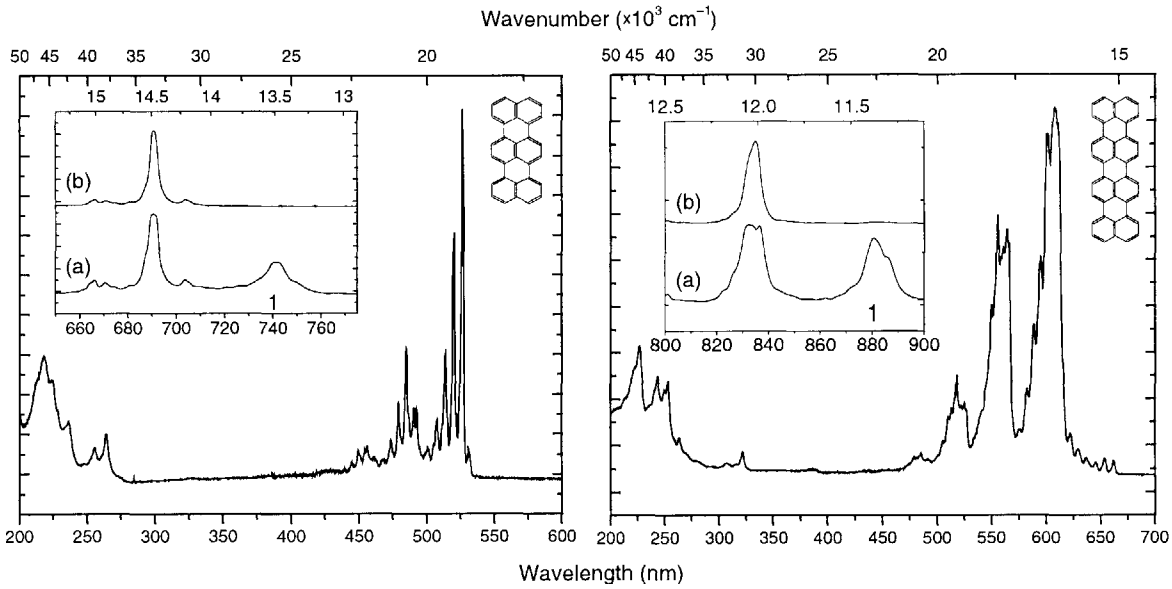

Fig. 5. Electronic matrix isolation spectrum of terrylene (left) and quaterrylene (right) in an inert neon matrix. The inserted panels show the absorption features of stable cations (plus symbols) and anions (minus symbols). Lines (a) in the panels show the electronic spectrum after UV irradiation (10.6 eV) in a neon (Ne) matrix, lines (b) show the UV irradiated spectrum in a neon/nitrogen dioxide (NO_2) matrix. Since the matrix is doped with the electron scavenger NO_2 we can discriminate between cation and anion features by comparing spectra (a) and (b).

as well as non-aromatic structures, such as carboxylic acids and amino acids.

Another theory for the fact that Viking did not find organic material is the destruction of organics by UV radiation. Stoker & Bullock (1997) have performed several laboratory experiments on organic degradation under simulated Martian UV conditions. These experiments show an organic decomposition rate of 8.7×10^{-4} g m^{-2} yr^{-1}. This rate exceeds the upper limit of infalling organics, 4×10^{-4} g m^{-2} yr^{-1}. This leads to the conclusion that the organic compounds, which reach the Martian surface as constituents of infalling micrometeorites, are probably destroyed by UV breakdown as rapidly as they are added.

Non-aromatic organic structures will be destroyed by UV radiation (Ehrenfreund *et al.* 2001). Polycyclic aromatic structures on the other hand are more resistant to UV radiation.

Fig. 5 shows the results of the matrix isolation spectroscopy of terrylene and quaterrylene in neon matrices (Ruiterkamp *et al.* 2002). Those PAHs are among the largest of their class measured under space-simulated conditions. Stable cations are formed when PAHs are subjected to Lyman-α UV radiation (10.6 eV) in inert matrices, but there is no spectroscopic evidence of fragmentation. Since the Martian atmosphere is opaque for radiation with energies higher than 6.5 eV (190 nm), all Lyman-α radiation will be absorbed. Thus PAHs with a high molecular mass, such as terrylene and quaterrylene, are expected to survive the radiation environment on Mars. From Earth-based tests with the Viking instruments (Biemann *et al.* 1977) it is shown that Viking should have been capable of detecting these molecules. This implies that other (chemical) mechanisms of destruction such as oxidation may also affect PAHs exposed to the Martian atmosphere.

Mars simulation chamber

Rationale

It is unclear why no traces of impacting organics have been found by Viking. It is likely that organic compounds are destroyed on the exposed surface, but may survive when protected by a greater depth of Martian dust. In order to determine the stability of specific organic compounds, laboratory simulations are a crucial step to understanding chemical pathways on the Martian surface.

In this context, an experimental programme was developed at the European Space Research and Technology Centre of ESA, ESTEC and Leiden University. The experimental research work includes the investigation of organic molecules subjected to simulated Martian atmospheres. An atmospheric simulation chamber in combination with a solar simulator is used to collect data on the combined effects of UV photoprocessing, atmospheric conditions and the presence/absence of oxidizing agents on organic molecules. All of 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 include aliphatic and aromatic hydrocarbons, fullerenes, amino acids, nucleo-bases and carbonaceous solids.

Technical set-up

The *Mars Simulation Chamber* (MSC), used for the experiments, is a 80 cm long, 60 cm high vacuum chamber, which will be filled with simulated Martian atmosphere, with 17 flanged portholes and a hinged door that allow access to the interior of the chamber (Figs 6 and 7).

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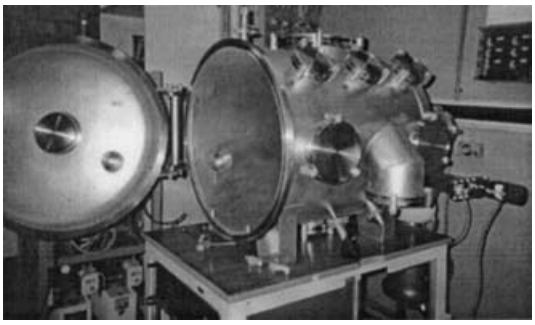

Fig. 6. Mars simulation vacuum chamber.

These flanged portholes are used for different purposes. To allow clean sample handling two differentially pumped rubber gloves, isolated from the exterior by two O-ring-sealed hinged blinds, were mounted on two ports at the side of the chamber. Above the gloves is another flange, which is used as a control window. A 1 kW solar simulator fitted with a 1 kW xenon lamp and a CaF_2 window are mounted perpendicular to the experiment plane, above the top port with a quartz window. The remaining flanges are used as feed-through flanges that allow controlled access of cryogenic fluids to the cold plate and shroud in the chamber, sampling of the interior gas by a GCMS apparatus and the introduction of gases into the chamber.

A turbo molecular pump, backed by a rotary vane pump is connected to the chamber. The rotary van pump is isolated from the chamber by a liquid nitrogen cold trap. The pumps can be separated from the chamber by an electric gate valve. An ion gauge and a pirani gauge monitor the pressure in the chamber.

The atmosphere in the chamber can be varied in pressure and in composition. The pressure maintained by the above-mentioned pumps varies from $\sim 5 \times 10^{-6}$ mbar to ambient pressure.

To simulate the current Martian atmosphere we use a mixture of N_2 (2.7% volume), Ar (1.6% volume), O_2 (1000 volumetric ppm), CO (500 volumetric ppm), H_2O (100 volumetric ppm) and CO_2 (rest of mixture). This gas mixture is transferred into the chamber as a premixed atmosphere, from gas tanks placed next to the chamber. The electromagnetic radiation environment can be changed in intensity and in spectral composition by means of a deuterium lamp with a spectral range of 115–600 nm, which can be mixed in with the solar simulator. This allows us to simulate other eras in Martian or terrestrial history.

The organic samples are introduced in the chamber in six sample holders (Fig. 7), fastened onto a copper ground-plate that allows temperature control by means of slush solutions that are pumped through the plate. The sample containers are 20 cm long stainless steel tubes with a diameter of 1.5 cm, which can be sealed with an O-ringed stopper. Three sample sites allow *in situ* measurements of the volatiles at three different heights in the containers, by means of stainless steel streams connected to a GCMS. The containers are welded to copper base-plates that are screwed on to the copper ground plate.

The temperature of the medium in the chamber can be cooled by means of a cold shroud positioned around the sample containers. Feed-through lines enable the cooling medium to enter the cold-shroud, allowing the temperature of the gases inside the chamber to be set between liquid nitrogen temperatures and room temperature. The temperature of the sample holders can be set within the same range.

The experimental protocol comprises three parts: (1) preparation of the chamber, (2) setting the experimental parameters and (3) *in situ* and post-processing measurements of the samples. During the preparation phase sample tubes are filled with a mix of Martian soil simulant, JSC-1 (Allen *et al.* 1998, 2000), organic compounds and oxidizing agents, and are attached to the copper ground-plate. The feed-through lines for the GCMS are connected to the sample holders and the chamber is pumped down to $\sim 5 \times 10^{-6}$ mbar. After closing the main gate valve the chamber is now filled with the simulation gases to a pressure of ~ 7 mbar. The experimental parameters that must be set prior to irradiation are the chamber temperature cycle, the sample temperature cycle and the *in situ* measurement protocol. During irradiation samples are taken from the volatiles inside the sample containers and fed to the GCMS in an automated fashion. Post-processing analysis of the samples by means of high-performance liquid chromatography (HPLC) is performed with a Shimadzu HPLC system, equipped with a fluorescence detector, a diode array detector and an auto-injector. All equipment used in the experiments, such as the transfer lines, sample holders and also the soil analogues, are sterilized (3 h at 500 °C) before use.

Complex organic samples

Specific organics will be embedded in either porous or compact Martian soil analogues or quartz beads. The recessed surface in the sample trays will be deep in order to simulate the effects of the various processes on organics according to their depth in the soil analogues.

Samples will be adsorbed on Martian soil analogues and quartz beads before exposure in the vacuum chamber. For these investigations, the sample holders will be charged with organic samples, such as:

(1) simple aliphatic species, such as pentane, hexane and octane;
(2) simple aromatic species, such as benzene, naphthalene and biphenyl;
(3) oxygen-bearing species, such as methanol and formic acid;
(4) nitrogen-bearing species, such as acetonitrile and propanetrile;
(5) simple amino acids, such as glycine and alanine;
(6) stable PAH molecules, such as tribenzo(a,g,m)coronene, hexa-peri-benzocoronene and ovalene;
(7) reactive PAHs, such as dibenzo(a,j)tetracene, pentacene and bisanthene;
(8) aza-, oxo-, thio-PAHs (since N and O are abundant elements in space);
(9) PAH isomers, such as benzo(a)pyrene/benzo(k)fluoranthene;

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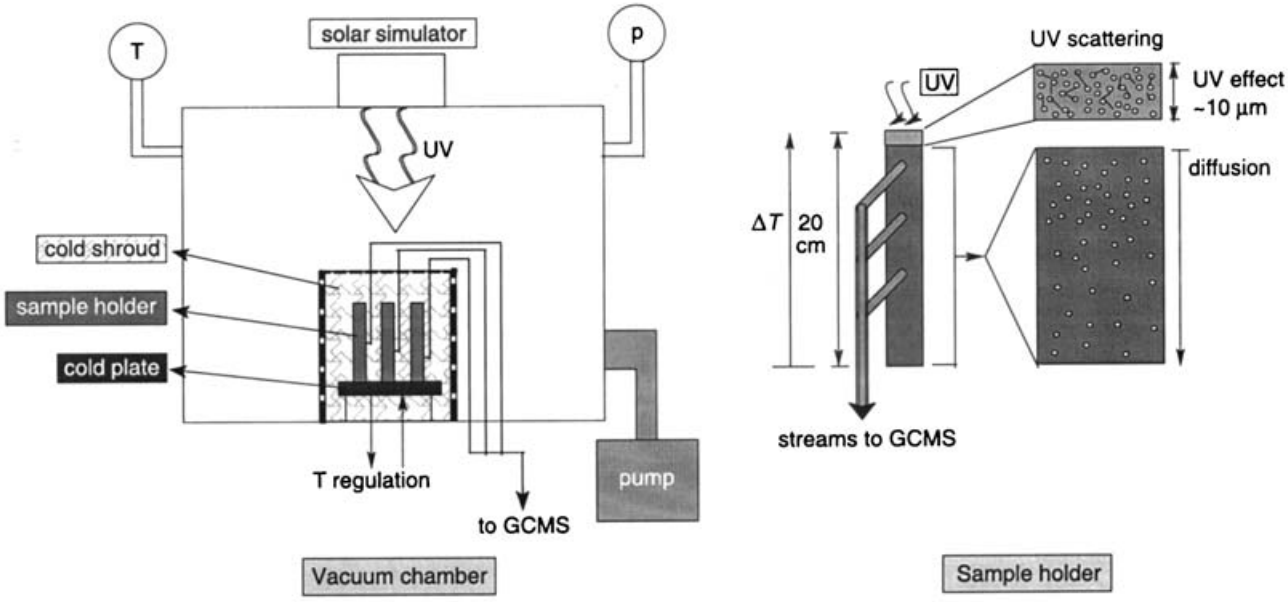

Fig. 7. Schematic outline of the Mars simulation chamber.

(10) fullerenes C_{60}, C_{70} and some of their hydrogenated compounds, as well as exohedral compounds containing Na, K and Mg;
(11) carbonaceous solids, such as AC or HAC; and
(12) kerogens and solid bitumens of different initial origin.

Experimental approach

The following experiments will be simulated in the vacuum chamber.

A. The effects of the Martian atmosphere. The chamber will be filled with gases simulating the evolution of the Martian atmosphere (CO_2, N_2 and Ar and traces of O_2 and CO). In order to simulate the clement phase of Mars' early atmosphere, pressures of 1–15 bar of CO_2 have been reported.
B. The effect of UV irradiation on organic molecules embedded in the soil. The solar UV flux may penetrate into the Martian soil down to a few millimetres due to scattering. We intend to simulate the UV irradiation with microwave discharge lamps and D lamps, which can be attached to the vacuum chamber. Filters will be used to simulate the variation of the solar UV flux between 190 and 280 nm, according to the O_3 content in the Martian atmosphere.
C. The effect of oxidation on organic molecules in the soil. As oxidizing agents we intend to use mostly H_2O_2, which will yield CO and CO_2 that escape the samples while breaking aliphatic bonds. Additionally, O_3 (present in the Martian atmosphere) will be added as gas in the chamber in order to study oxidation effects. O_3 fixation on Earth in the ground has been estimated to be 0.07 cm s^{-1} and therefore O_3 may be of relevance for the Martian soil.
D. The effect of thermal cycling on the surface. We shall reproduce the thermal (e.g. 180–280 K) cycling and measure the evolution and thermal degradation products of embedded organics. In the higher temperature range, the sublimation rates of the more volatile compounds will be significant.

Future missions

Below, several Mars missions that will be launched in the near future are briefly described. All of these missions will include instruments capable of searching for evidence of water and of early (or even present) life.

Mars Express

Mars Express (ESA) will be launched in June 2003. Its main goal is to study the cycle of water from orbit and drop a lander (Beagle 2) on to the Martian surface. The Mars Express orbiter is equipped with seven scientific instruments and will perform remote sensing experiments to investigate the Martian atmosphere, internal structure and mineralogy. The Beagle 2 lander will perform experiments in exobiology and geochemistry. Although the orbiter has a range of sophisticated instruments on-board as well, only the lander instruments will be described here, since the lander instruments are directly related to the research performed with the Mars Simulation Chamber.

In the *gas analysis package* (GAP), CO_2 is generated by heating samples of soil or rock in the presence of oxygen. Under the conditions used in this experiment package all forms of carbon convert to CO_2, either by decomposition (carbonates) or by combustion. The carbon isotopic composition of the CO_2 will be measured with a mass spectrometer. This mass spectrometer will also study other elements and look for methane in samples of the atmosphere.

In addition to several *environmental sensors*, the main instrument package on the Beagle 2 lander is the *PAW*

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instrument package, which is mounted at the end of the robotic arm. It consists of several small instruments.

- *Two stereo cameras* to construct a three-dimensional model of the area within reach of the robotic arm.
- A *Microscope* with a resolution of 4 μm, to reveal the shape and size of dust particles, the roughness and texture of rock surfaces and the microscopic structure of rocks.
- A *Mössbauer spectrometer* to investigate the mineral composition of rocks and soil by irradiating rock and soil surfaces with gamma-rays, and then measuring the spectrum of the gamma-rays reflected back.
- An *X-ray spectrometer* to measure the amounts of elements in rocks by bombarding exposed rock surfaces with X-rays.
- The *Mole* (PLUTO for PLanetary Underground TOol) to collect soil samples from underneath rocks for return to the GAP.
- A *corer/grinder* to drill down 4 mm to acquire a sample of rock powder for analysis in the GAP.

2003 Mars Exploration Rovers

The NASA 2003 Mars Exploration Rovers mission will also be launched in 2003. The mission consists of two identical rovers, landing at different sites, which can drive up to 100 m per day to search for evidence of liquid water in the past. Rocks and soil will be analysed with five different instruments on each rover: a panoramic camera, a miniature thermal emission spectrometer, a Mössbauer spectrometer, an alpha-particle X-ray spectrometer and a microscopic imager.

2005 Mars Reconnaissance Orbiter

The Mars Reconnaissance Orbiter (MRO) will make high-resolution measurements of the surface from orbit. It will be equipped with a visible stereo imaging camera (HiRISE) with a resolution of 20–30 cm and a visible/near-infrared spectrometer (CRISM) to study the surface composition. Also on-board will be an infrared radiometer, an accelerometer, and a shallow subsurface sounding radar (SHARAD).

Its main goals will be to collect data on the gravity field, evidence of past or present water, weather and climate, and landing sites for future missions.

PREMIER

PREMIER (Programme de Retour d'Echantillons Martiens et Installation d'Expériences en Réseau) is a French (CNES) programme with two goals:

- participation in the Mars sample return project (MSR) through co-operation with NASA and
- deployment of a network of Martian landers in co-operation with European partners (NetLander project).

The science goals of PREMIER are to reveal new data on the historical and contemporary geology, climate and biology.

The 2009 NETLANDER mission

The CNES-Europe NetLander Mission will consist of a network of four geophysical and meteorological landers and is part of the PREMIER mission.

This mission will allow us to study:

- deep internal structure;
- global atmospheric circulation;
- planetary boundary layer phenomena;
- subsurface structure at the kilometre scale, down to water-rich layers;
- surface mineralogy and local geology; and
- alteration processes and surface–atmosphere interaction.

Aurora

Within the framework of the Aurora programme, ESA is performing assessment studies of two Flagship missions, which are major milestones to advance the scientific and technical knowledge in preparation for a human mission; and two Arrow missions, which are typically less complex and cheaper technology missions intended to reduce the risk involved in the more complex Flagship flights. The approved Flagship mission studies are the Exo-Mars Mission and the Mars Sample Return Mission.

The Exo-Mars mission

The Exo-Mars mission, an exobiology mission, searching for life outside the Earth, will investigate the Martian biological environment before other landings take place. The mission will consist of an orbiter and a rover. Its payload will include a drilling system, as well as a sampling and handling device integrated with the package of scientific instruments.

The Mars Sample Return mission

This mission is composed of a vehicle that will deliver a descent module and an Earth re-entry vehicle into a Mars orbit. The descent module will carry a landing platform equipped with a sample collecting device and an ascent vehicle. This ascent vehicle will return a small container with the sample into a low-altitude circular Mars orbit for a rendezvous with the Earth re-entry vehicle. The re-entry capsule containing the sample will be returned on a ballistic trajectory into the Earth's atmosphere.

Perspectives

The Mars Simulation Chamber is used to validate measurements to be made by Beagle 2, and other future spacecraft missions to Mars. Using the MSC we will try to answer a range of questions on the subject of the apparent absence of organic compounds on Mars. Techniques to be used include gas analysis, environmental sensors, HPLC, spectroscopy and other analytical techniques.

We shall also assess the sensitivity of instruments for the detection of minerals and organic compounds of exobiological relevance in Martian analogue soils (mixed under controlled conditions with traces of these organics). The results concerning the simulation of complex organics on Mars, as well as lander instrument chamber simulations will be included in a database to serve for the interpretation of Beagle 2 data and other future Mars missions.

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The following questions, concerning ground-based measurements, will be examined in this project.

- *There is obviously organic material delivered to Mars by meteorites and IDPs – why do we not see it?*

The effects of several oxidizing agents will be examined as well as the chemical processing of surface samples owing to a combination of parameters.

- *It is assumed that the organic material is destroyed by oxidizing agents – what is their penetration depth in the regolith?*

During the experiments we will estimate the depth to which it is necessary to drill, in order to find intact organics.

- *Water has been found by the Mars Odyssey orbiter – what is the influence of water on the destruction and reaction pathways of organics?*

Until a few years ago it was only assumed that there was perhaps water on Mars close to the surface. Since the presence of water in this depth has now been confirmed by the Mars Odyssey, its effect on the organic material in the soil cannot be neglected.

The results of the experiments can also provide constraints for the observations from orbit, such as spectroscopy of minerals, measurements of the water cycle, frost and subsurface water, the CO_2 cycle and the landing site selection.

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