Organics on Mars : Laboratory studies of organic material under simulated martian conditions

Kate, Inge Loes ten

Citation

Kate, I. L. ten. (2006, January 26). *Organics on Mars : Laboratory studies of organic material under simulated martian conditions*. Retrieved from https://hdl.handle.net/1887/4298

Chapter 1

General introduction

This thesis describes the results of laboratory investigations of the reactions of certain amino acids and microorganisms under simulated martian surface conditions. An overview of the current state of knowledge of the planet Mars is given in this chapter. Furthermore the rationale behind the investigations is described. The research and its results are summarised at the end of this chapter.

1. MARS

Mars, named after the Roman god of War, is the fourth planet in our Solar System as seen from the Sun, with an average distance of 227.9 million kilometres (1.52 astronomical units, AU), see Fig. 1.

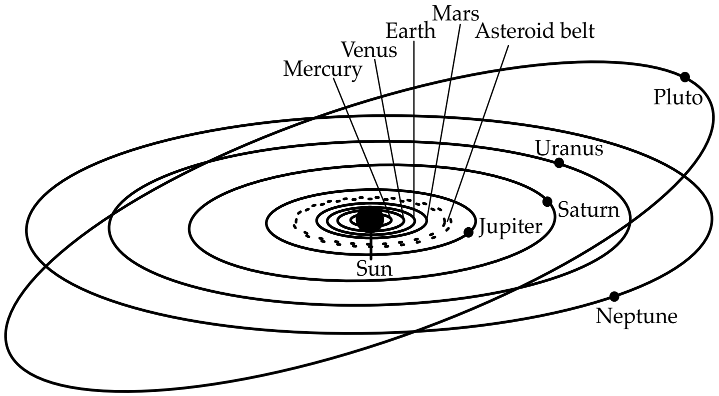

Fig. 1. Schematic overview of the Solar System (not on linear scale).

With a diameter of 6794 km, approximately half the size of the Earth, Mars is the seventh largest planet in the Solar System. Mars' orbit is much more elliptical than the Earth's, causing among other things a large temperature difference between perihelion and aphelion (the closest point towards and furthest point away from the sun). The average temperature on the surface is around 218 K (-55 °C), and can vary between 140 K (-133 °C) on the poles in winter and 300 K (+27 °C) around the equator on the day side in summer. Table 1 gives a comparison of characteristic parameters of the present day Mars and Earth. Fig. 2 shows a Hubble picture of Mars.

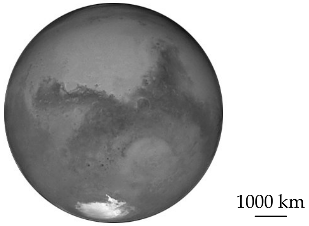

Fig. 2. Mars during its closest approach to Earth in 60,000 years. This picture was taken in August 2003 by the Hubble Space Telescope in orbit around the Earth, and is the most detailed view of Mars ever taken from Earth. Visible features include the south polar cap in white at the image bottom, the circular Huygens crater just to the right of the image centre, Hellas Impact Basin - the large light circular feature at the lower right, planet-wide light highlands dominated by many smaller craters, and large sweeping dark areas dominated by relatively smooth lowlands. Credit: J. Bell (Cornell U.), M. Wolff (SSI) *et al.*, STScI, NASA.

Table 1. Characteristic parameters of Mars and the Earth[§]

Characteristics	Mars	Earth
Equatorial radius	3397 km	6378 km
Approximate mass	0.64×10^{24} kg	5.97×10^{24} kg
Surface gravity	3.71 m s^{-2}	9.80 m s^{-2}
Average density	3933 kg m^{-3}	5515 kg m^{-3}
Mean distance from the Sun	227.9 million km (1.52 AU)	149.6 million km (1 AU)
Orbital eccentricity	0.09	0.02
Orbital period	686.98 days	365.26 days
Rotational period	24 h 37 min	23 h 56 min
Surface temperature	mean: 210 K (-63 °C); range: 140 K to 300 K (-133 °C to +25 °C)	mean: 288 K (15 °C); range: 184 K to 330 K (-89 °C to +57 °C)
Atmospheric composition (main gases, % by moles)	95.3% CO_2, 2.7% N_2, 1.6% Ar, 0.15% O_2, 0.08% CO, 0.03% H_2O	78.1% N_2, 20.9% O_2, 0.9% Ar, traces CO_2, CH_4, Ne, He, Kr, H
Atmospheric pressure	average 6.36 mbar (4-9 mbar)	average at sea level 1014 mbar
Number of satellites	2 (Phobos, Deimos)	1 (Moon)

[§] http://nssdc.gsfc.nasa.gov/planetary/factsheet/marsfact.html

The current state of knowledge about Mars has been obtained in several ways. Observations of the atmosphere and surface have been made by ground and space based telescopes. Meteorites that are believed to be of martian origin are analysed for their chemical and geochemical composition. These meteorites are called SNC meteorites, named after the collection site of the first three meteorites believed to be from Mars (Shergotty, Nakhla and Chassigny). Moreover, Mars has been visited by many spacecraft (orbiters and landers), with varying degrees of success (see Table 2, p. 16,17). These close investigations have shown that our neighbouring planet has had an interesting history and that it likely harbours water in its subsurface.

2. MARS' INTERIOR

Mars has a relatively low density (3933 kg m^{-3}) compared to the other terrestrial planets (Earth (5515 kg m^{-3}), Venus (5243 kg m^{-3}) and Mercury (5427 kg m^{-3})), suggesting a relatively large fraction of lighter elements, such as sulphur.

Core

Like the Earth's, the martian core is assumed to consist mainly of iron and small amounts of nickel. Various compositional models suggest a core with a radius between 1500 and 2000 km and fractional mass of 15 to 30 %. However, from what is currently known of the geophysical and geochemical composition of Mars, various compositions could be possible, ranging from a nearly pure iron core comprising 15 % of the planet's mass, or a iron-nickel core of ~40 % of Mars' radius, to a core containing 34 weight% sulphur, constituting 24 % of the planet's total mass and 60 % of its radius (Schubert *et al.*, 1992, Longhi *et al.*, 1992, and references in both).

Observations from the Magnetometer and Electron Reflectometer (MAG-ER) instrument on the Mars Global Surveyor (MGS) showed that Mars currently does not have a global magnetic field. However, these observations suggest that Mars may have had a magnetic field in the distant past. This magnetic field would have been caused by an active core dynamo (Acuña *et al.*, 2001) that ceased to operate ~4 Gyr (10^9 year) ago (Acuña *et al.*, 1999). However, regions with a small magnetic field still exist. These fields are caused by the interaction of the solar wind with the atmosphere (Connerney *et al.*, 2001), and by magnetised crust that formed when Mars still had a global magnetic field (Acuña *et al.*, 1999).

Like Earth, Mars is influenced by the gravitational pull of the Sun. This causes a solid body tide with a bulge toward and away from the Sun. However, for Mars this bulge is much smaller than for the Earth. By measuring this bulge in the Mars gravity field, the flexibility (also called the solar tidal deformation) of Mars can be determined. As measured by Mars Global Surveyor (MGS) radio tracking, this deformation shows that it is large enough to rule out a solid iron core and indicates that at least the outer part of the core is liquid (Yoder *et al.*, 2003).

Mantle and crust

The thickness of the mantle and the crust can only be estimated from indirect evidence, which leads to quite some variation between the existing models. The thickness of the mantle is estimated to be 1500 to 2100 km (Schubert *et al.*, 1992). The mantle can be subdivided into an upper part (900-1100 km thick) and a lower part (from the base of the upper part to the core). The estimates for the thickness of the crust vary widely between values of 9 km and 130 km for the Hellas basin only, and between 28 and 150 km for a global average. Models based on the composition of the SNC meteorites, however, predict that the densities used for these thickness estimates are much too low (Schubert *et al.*, 1992, Longhi *et al.*, 1992, and references therein).

The elemental composition of the mantle and the crust is estimated to be 36.8 to 44.4 % silicon dioxide (silica, SiO_2), 0.1 to 0.3 titanium dioxide (TiO_2), 3.0 to 6.4 % aluminium oxide (Al_2O_3), 0.4 to 0.8 % chromium oxide (Cr_2O_3), 27.4 to 32.7 % magnesium oxide (MgO), 15.8 to 26.8 % iron oxide (FeO), 0.1 to 0.5 % manganese oxide (MnO), 2.4 to 5.2 % calcium oxide (CaO), 0.1 to 1.4 % sodium oxide (Na_2O), 0.001 to 0.9 % water (H_2O) and 60 to 1200 part per million potassium (K). In addition, a range of minor and trace elements is present in the martian mantle (Longhi *et al.*, 1992, and references therein). The mineralogical composition of Mars is somewhat similar to that of the Earth; the most abundant mineral in the upper mantle is olivine ($(Mg,Fe)_2SiO_4$) and the next most abundant is orthopyroxene ($(Mg,Fe)SiO_3$) (Longhi *et al.*, 1992, Mustard *et al.*, 2005).

3. MARS' SURFACE

The history of Mars can be subdivided into three periods, the Noachian, the Hesperian, and the Amazonian, in chronological order. These periods represent the major periods of geologic activity and are named after the surface region formed during that period (Tanaka *et al.*, 1992). From a geology point-of-view Mars is very different from the Earth. Mars has two very different hemispheres, with an abrupt change in elevation of 2-5 km kilometres between the old and heavily cratered highlands of the southern hemisphere and the younger, less cratered northern lowlands, a phenomenon known as hemispheric dichotomy (Smith *et al.*, 1999). The majority of the southern highlands are formed during the Noachian period. The northern lowlands, are mostly covered by lava flows and sediments of late Hesperian and Amazonian age (Tanaka *et al.*, 1992). The surface of Mars has more distinguished features, such as the volcano Olympus Mons (with a height of 24 km the largest mountain in the Solar System), Tharsis (a 4000 km long bulge with an elevation of 10 km), and Valles Marineris (a system of canyons with a depth between 2 and 7 km). Finally, Hellas Planitia, a 6 km deep impact crater with a 2000 km diameter, can be found in the southern hemisphere. Recent high resolution observations show channels indicative of past water flows on Mars, see Fig. 3. A molten rocky mantle and a thin crust build up the surface of Mars. Four major processes have shaped planet Mars in the past: plate tectonics, volcanism, impact cratering and erosion.

Plate tectonics

Recent observations have shown that the regional crustal magnetic field in Meridiani has characteristics that are, on Earth, unique to plate tectonics. This supports the idea that the crust of Mars is composed of plates formed in an early era, in the presence of a core dynamo. However, the thickness and size of the southern highland crust have led to ceasing plate motions, by growing beyond a critical fraction (0.5) of the planet's surface (Connerney *et al.*, 2005; Lenardic *et al.*, 2004; Banerdt *et al.*, 1992).

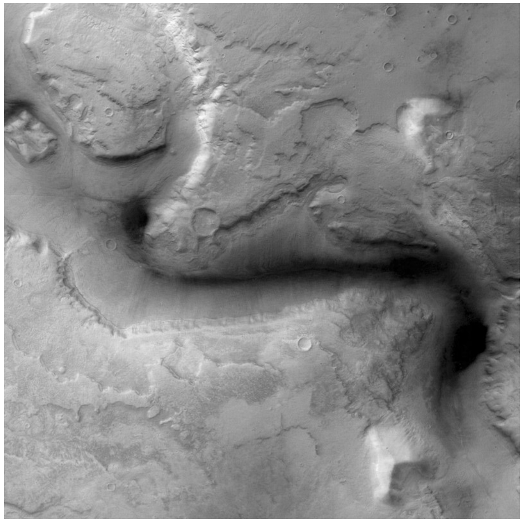

Fig. 3. Past water channels on Mars. This picture was taken by the High Resolution Stereo Camera (HRSC) onboard ESA's Mars Express orbiter, in colour and 3D, in orbit 18 on 15 January 2004 from a height of 273 km. The location is east of the Hellas basin at 41° South and 101° East. The area is 100 km across, with a resolution of 12 m per pixel, and shows a channel (Reull Vallis) once, almost certainly, formed by flowing water. The landscape is seen in a vertical view, North is at the top. Credits: ESA/DLR/FU Berlin (G. Neukum).

Volcanoes

Mars has the largest shield volcanoes in the solar system. Shield volcanoes are tall volcanoes with broad summit areas and low-sloping sides. The large scale of these volcanoes is caused by the fact that Mars lacks plate tectonics. Mars also has a wide range of other volcanic features, including large volcanic cones, unusual patera structures (flat, ash-shield volcanoes), mare-like volcanic plains, and a number of other smaller features. Volcanic features appear mostly in three regions. The largest part of those volcanoes can be found in Tharsis, consisting of 12 large volcanoes and a number of smaller ones, among which Olympus Mons and Alba Patera. Alba Patera is the largest volcanic structure on Mars, an area with a low elevation, but a large caldera, over 1500 km in diameter. A much smaller cluster of three volcanoes lies in Elysium, and a few paterae form the third region near the Hellas impact basin. New data from the High Resolution Stereo Camera (HRSC) onboard Mars Express indicate very recent volcanic activity, suggesting that the volcanoes are potentially still active today. The data show repeated activation and resurfacing of five major volcanoes, with phases of activity as young as two million years (Neukum *et al.*, 2004).

Impact cratering

Impact cratering is observed on the surface of all terrestrial planets. On Mars, craters occur in all sizes, from a few meters up to thousands of kilometres in diameter, like giant basins as Hellas, 2400 km, and Argyre, 1792 km across. More craters appear on the southern highlands than on the northern lowlands, which may imply that the southern areas are older than the northern. The southern cratered highlands are thought to have formed around 3.5-4 Gyr ago; the northern lowlands were assumed to be much younger, through dating by extrapolating recent lunar and terrestrial impact rates to Mars. Recent studies, however, imply that this method may have caused an underestimation of the age, and that the northern lowlands are probably of the same age as the southern highlands (Chappelow and Sharpton, 2005).

Erosion

On the surface of Mars several erosive processes play a role, such as weathering, mass wasting by creep or land sliding, precipitation-driven runoff, erosion by ground water seepage, and wind-induced (aeolian) erosion and deposition. Several regions on Mars show topographic features that are suggested to have resulted from aeolian erosion, such as large-scale linear grooves and ventifacts (microscale pits in rocks) (e.g. Bridges *et al.,* 1999). Aeolian dust may be composed of fine-grained surface materials, like weathered rock particles and regolith, as well as material injected in the atmosphere by impacts and volcanic eruptions. Deposition of dust forms features like dunes and crater filling. Although Mars has a very thin atmosphere large dust storms occur on the surface. These dust storms are produced by high velocity seasonal winds correlated with solar heating of the surface and lead to high surface erosion. A recently discovered form of water erosion by the Mars Orbiter Camera (MOC) on MGS is the so-called gully (see section 5).

Soil

The surface of Mars is covered by a fine soil (see Fig. 4) that contains silicon, iron, aluminium, magnesium, calcium, titanium and is relatively rich in sulphur and chlorine, compared to terrestrial soils. Mars' red colour is caused by oxidation of iron in the soil and in rocks, when exposed to oxidants formed among others by photochemistry in the atmosphere. These and other oxidants are present in the soil as well, and may be one of the causes of the lack of organic material (e.g. Yen *et al.*, 2000). High concentrations of minerals, such as chlorine and sulphur salt-minerals, magnetically active minerals and jarosite (see section 5) have been detected. On the other hand, the soil seems to lack carbonates and clay minerals. (For reviews see Squyres *et al.*, 2004 a, b; Banin, 2005, and references therein; Yen *et al.*, 2005).

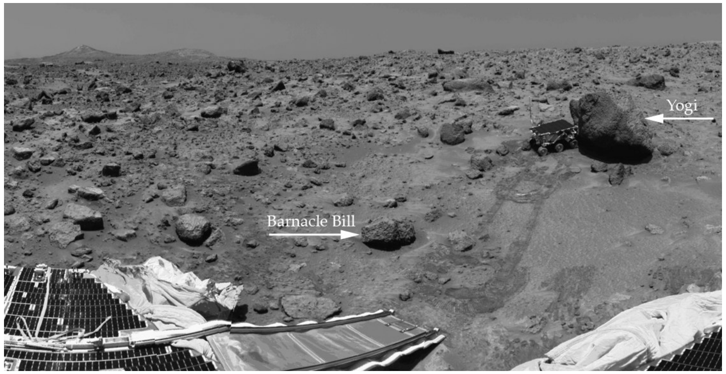

Fig. 4. The surroundings of the Sagan Memorial Station on Mars, as observed by Mars Pathfinder. The big rock on the fine grained soil on the right is called Yogi and just to its left is the robot Sojourner Rover taking measurements of it. Other now-famous rocks are also visible including Barnacle Bill. Credit: IMP Team, JPL, NASA.

4. MARS' ATMOSPHERE

The major component (95.3 %) of the martian atmosphere is carbon dioxide (CO_2, Kuiper, 1955). Other major gases in Mars' atmosphere are nitrogen, argon, oxygen and carbon monoxide (Owen, 1992). Water is a minor constituent, varying between 10 and 1000 parts per million (ppm, Encrenaz *et al.*, 2004a). Several other trace gases have been detected in the martian atmosphere, including hydrogen peroxide (20-50 parts per billion (ppb), Clancy *et al.*, 2004; Encrenaz *et al.*, 2004b) and methane (CH_4, 5 ppb, Krasnopolsky *et al.*, 2004; Formisano *et al.*, 2004). The detection of CH_4 is debated, but important, due to its relation to biological processes and to non-equilibrium geochemistry. In contrast to the Earth's atmosphere, the martian atmosphere does not contain a significant amount of ozone (O_3, 40-200 ppb, Owen, 1992), which acts on Earth as protection against ultraviolet radiation. The surface pressure ranges from 9 mbar in deep basins to 1 mbar at the top of Olympus Mons, with an ave-rage of 7 mbar, which is still thick enough for strong winds and dust storms to occur. There is a weak greenhouse effect, just enough to raise the surface temperature by a few degrees. This temperature rise is not sufficient to establish and maintain a surface temperature where liquid water can exist. If the temperature is high enough for water-ice to melt, the atmospheric pressure is so low that water-ice directly evaporates. It is thought that Mars had a much denser atmosphere in the past. Due to its small mass and weak gravity Mars was not able to retain its atmosphere. Sputtering by solar wind may have additionally eroded the atmosphere, since Mars has lost its global magnetic field and corresponding protective magnetosphere. Mars' small size and lack of plate tectonics and active volcanoes prevent the CO_2 that is locked as carbonates, from being recycled back into the atmosphere. The current CO_2 cycle is predominantly caused by the seasonal condensation and sublimation in the polar regions (Owen, 1992).

5. WATER ON MARS

Polar ice caps
Mars has ice caps at the north and south pole, both growing and receding with the seasons. The north pole has a residual summer cap consisting of nearly 100 % water-ice, covered by a seasonal cap of CO_2 ice (Feldman *et al.*, 2003; Byrne and Ingersoll, 2003), and is surrounded by sand dunes. The south pole consists of layered deposits thought to be composed of dust and a mixture of CO_2 ice and water-ice (Bibring *et al.*, 2004; Titus *et al.*, 2003). Like the north pole, the south pole is covered with a seasonal CO_2 cap. The residual cap on the south pole shows a wider variety of geologic features than the cap on the north pole, indicating an asymmetry in the polar climates of Mars (Thomas *et al.*, 2000).

Equatorial regions
In 2002 the High Energy Neutron Detector, the Neutron Spectrometer and the Gamma-Ray Spectrometer on board Mars Odyssey identified hydrogen rich regions in both poles as well as in regions closer to the equator. Modelling suggests that tens of centimetres thick water-ice rich layers, similar to permafrost layers on Earth, exist in these regions, buried beneath hydrogen-poor soil (Mitrofanov *et al.*, 2002; Feldman *et al.*, 2002; Boynton *et al.*, 2002). The existence of such permafrost layers underneath the surface has been suggested already since the Viking missions (Bianchi and Flamini, 1977).

As described earlier, a gully can be formed by water flow, for example caused by the melting of snow deposits on the poles (Christensen, 2003). Most of the gullies detected on Mars are found in the south, occurring in regional clusters within the walls of a few impact craters, south polar pits and martian valleys (see Fig. 5). Their appearance can be explained by processes associated with ground water seepage and surface runoff. Also shallow and deep aquifers in the martian subsurface are thought to play a role in the formation of the gullies (Heldmann and Mellon, 2004). From the lack of impact craters overlaying the gullies and the relationship of the gullies to the underlying ground, the gullies are estimated to be relatively young, younger than a million years (Malin and Edgett, 2000).

Both Spirit and Opportunity discovered haematite at the surface of Mars, a mineral that on Earth is usually formed in the presence of water. Furthermore the instruments on Oppor-

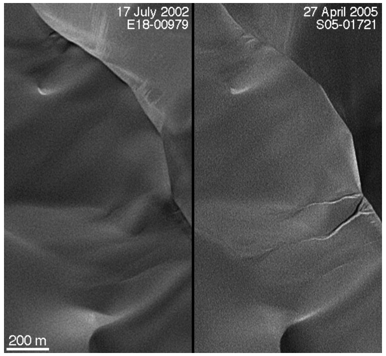

Fig. 5. Formation of a gully. This pair of images is taken by the Mars Orbiter Camera (MOC) onboard the Mars Global Surveyor. The images show a couple of gullies that have been formed during ~1.4 Mars years on a dune in an unnamed crater in the Hellespontus region, west of Hellas Basin. The 2002 image was obtained with the incident sunlight coming from a lower angle, relative to the horizon, than the 2005 image. If the gullies would have been present in 2002 their appearance would have been sharper and more pronounced than they are in the 2005 image. Credit NASA/JPL/MSSS/ASU

tunity detected high levels of sulphate salts (jarosite, an iron sulphate mineral), which on Earth would normally form in water. Opportunity also found rocks containing small spherules, nicknamed Blueberries, and indentations that point to modification by liquid water (Klingelhöfer *et al.*, 2004; Rieder *et al.*, 2004; Squyres *et al.*, 2004c).

6. LIFE ON MARS

From what is known on Earth, life needs water and life is sensitive to ultraviolet radiation. The absence of liquid water at the surface of Mars and the strong radiation environment, caused by the thin atmosphere and the lack of ozone, make Mars hostile to known terrestrial life. Several attempts have been undertaken to search for life on or from Mars. The Viking mission (see Table 2) was designed to search for evidence of life, as was the failed Beagle 2 mission. On Earth the martian meteorite ALH84001 has been examined for organic material and fossils of early, very small life forms (McKay *et al.*, 1996). Recent investigations by the Opportunity Rover in Meridiani Planum show aqueous and aeolian depositions in regions that were dry, acidic and oxidising. The measurements suggest that Meridiani Planum may have been habitable during at least part of the interval when the depositions took place (Knoll *et al.*, 2005).

The Viking Mission

The Viking mission consisted of two spacecraft, Viking 1 and Viking 2, both composed of an orbiter and a lander (Soffen, 1977). Viking 1 landed on July 20, 1976 at Chryse Planitia (22.48 ° N, 49.97 ° W), and Viking 2 at Utopia Planitia on September 3, 1976 (47.97 ° N, 225.74 ° W). The main goals of the mission were to obtain high resolution images of the martian surface, to characterise the structure and composition of the atmosphere and surface, and to search for evidence of life (Biemann *et al.*, 1977). The biology experiments initially could have pointed to life in the martian soil. Based on these results the presence of a process that would destroy organic material in the near surface environment has been suggested. The results of the molecular analysis experiment, however, pointed towards the absence of organic compounds in the martian soil (see section 7). For a more in-depth description of the Viking missions see Chapter 2.

ALH 84001

Meteorite ALH84001, named after its discovery location Allan Hills on Antarctica, is thought to come from Mars. In 1996 it was reported that ALH84001 contained possible evidence for life on Mars, in the form of biogenic fossils, polycyclic aromatic hydrocarbons (PAHs) and magnetite (Fe_3O_4) (McKay *et al.*, 1996). This claim has been the subject of intense debates (Jull *et al.*, 1998), but more recently conclusions have been drawn that the fossils are probably artefacts and that magnetite and PAHs found within ALH84001 are terrestrial contamination (Barrat *et al.*, 1999), or have been produced inorganically, without biological influences (Kirkland *et al.*, 1999; Golden *et al.*, 2000; Thomas-Keprta *et al.*, 2001, 2002; Zolotov and Shock, 2000).

Future endeavours for life detection

Mars may have had better conditions to host life in the past. If life would have existed on the surface or in the near subsurface, remnants of this extinct life may be still present. From Earth it is known that life can survive under extreme conditions; early life on Mars could also have evolved into extreme life forms still present in the subsurface or underneath rocks. In the near future several missions will be launched to land on the surface in order to conduct life-detection experiments. The Phoenix lander is designed to land in the north polar region (2007), the Mars Science Laboratory is to be launched in 2009, and ExoMars, the first European Mars rover is foreseen to be launched in 2011. These landers and rovers are expected to carry suites of instruments that are able to detect organic material in the ppb/ppt range and possible traces of life on Mars. In the context of these missions 'planetary protection' issues, such as contamination of martian soil with terrestrial bacteria, have to be evaluated (Rummel and Billings, 2004).

7. Rationale and topic of this research

As described in the previous section no organic material or any remnants have been detected on the surface of Mars. Organic material has, however, been detected in the interstellar medium (Millar, 2004; Ehrenfreund and Charnley, 2000; and references in both), in comets (see Crovisier, 2004, for a review), meteorites (Sephton, 2002; Botta and Bada, 2002; and references in both) and interplanetary dust particles (Schramm *et al.*, 1989; Flynn, 1996). A major source of organic material on the primitive Earth and Mars could have been delivered from space via comets and small interplanetary dust particles (e.g. Chyba *et al.*, 1990). Mars had a history of being bombarded like the Earth, with an estimated annual planet-wide amount of organic material, incorporated in dust particles, impacting intact on the surface in the order of 10^6 kg per year (Flynn, 1996). This extramartian material provides one

possible source of organic material on the surface of Mars. Endogenous production of organic material on Mars cannot be excluded. Several mechanisms for endogenous production of organic material on early Earth have been suggested, such as lightning, coronal discharge, UV radiation, and atmospheric shocks. Some of these processes could have played a role on early Mars as well (Chyba and Sagan, 1992).
The fact that no organic material has been detected on the surface of Mars leads to several questions:

- » Is infalling extramartian material overheated or burned during atmospheric entry?
- » Is extramartian material delivered intact, but destroyed on the surface by UV radiation?
- » Are there oxidising processes occurring in/on the surface that destroy organics?
- » What role does water play in the destruction of organic material?
- » Can organic material be detected underneath the martian surface or within rocks?
- » Were the Viking instruments sensitive enough?

It is possible that the Viking GCMS may have failed to detect certain types of organic material. Glavin *et al.* (2001) reported that the pyrolysis products (mainly ethylamine) of several million bacterial cells per gram of martian soil, would have fallen below the detection limits of the Viking GCMS, which had already been suggested by Klein (1978, 1979), but was never confirmed with experimental data. For a review see Klein *et al.* (1992). Benner *et al.* (2000) concluded that organic molecules, such as benzenecarboxylates, oxalates and perhaps acetates are likely to have been formed on the martian surface via oxidation of impacted organic material. These compounds are not directly detectable by GCMS. Instruments with higher sensitivity (in the ppt range) using higher pyrolysis temperatures may be more successful in the future to pick up the signature of trace organics.
Next to the in-situ research as carried out by the Viking landers, Earth-based laboratory research and theoretical work has tried to answer some of these questions. A few related projects are briefly described. Oró and Holzer (1979) investigated the photolytic degradation of glycine, adenine and naphthalene adsorbed on powdered quartz, under UV radiation from a mercury discharge lamp (~245-275 nm) at room temperature (25 °C), 10 °C and 4 °C. They also investigated the oxidative effect of the presence of oxygen during irradiation. Their results indicate that only naphthalene breaks down significantly due to UV radiation, and that glycine and adenine only degrade in the presence of oxygen, implying that in the presence of oxygen, UV exposure enhances the oxidative degradation of the examined compound. Stoker and Bullock (1997) investigated photolytic degradation of glycine under UV radiation from a xenon lamp (~200-800 nm), when mixed with a Mars soil analogue under a Mars-like atmosphere. From their experiments they concluded that, even in the absence of oxidants, the surface conditions are severe enough to break down organic compounds at a faster rate than the rate at which they arrive at the surface. Yen *et al.* (2000) showed that, under a simulated martian atmosphere, superoxide radicals form on Mars-analogue surface minerals

when exposed to UV radiation. These radicals could play an important role in destroying organic material on the surface. Quinn *et al.* (2005a,b) have investigated the photochemical stability of carbonates under simulated Mars conditions as well as the aqueous decomposition of organic compounds in martian soils. From these experiments it is concluded that soil and water-ice may serve as a sink for photochemically produced oxidising species resulting in accelerated organic decomposition kinetics during wetting events. Their results also suggest that the apparent absence of carbonate deposits on the martian surface could be due to UV photodecomposition of calcite.

The research described in this thesis focuses on the stability of organic material on the surface of Mars, where UV radiation, atmosphere and temperature play a role. It is practically impossible to fully recreate planetary conditions in the laboratory. However, one of the advantages of experimental work is that simultaneously occurring effects may be studied separately, thus allowing us to investigate individual processes that give crucial insights into the complex multiparameter destruction processes of organics on Mars.

8. OUTLINE OF THIS THESIS

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. In order to determine where and what those missions should be looking for, laboratory experiments under simulated Mars conditions are crucial.

Chapter 2 describes experiments that are performed in support of future Mars 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. An overview on future missions is given stressing the relation between space missions and laboratory simulations.

Experiments performed to study the stability of thin films of two amino acids against UV irradiation are described in **Chapter 3**, together with a technical description of the equipment. The data obtained through these experiments are used to predict the survival time of these compounds on and in the martian regolith. We show that thin films of glycine and D-alanine are expected to have a half-life of 22 ± 5 hours and of 4 ± 2 hours, respectively, when irradiated with Mars-like UV flux levels. Fig. 6 shows the infrared (IR) spectra of glycine and D-alanine and the destruction after ~50 hours of UV irradiation. A model of amino acids embedded in the regolith with a mixing ratio of 1 ppb, shows that they would survive for as long as 10^7 years, when considering UV effects only.

Chapter 4 contains follow-up experiments to Chapter 3, describing the measured effects of two parameters, a CO$_2$ atmosphere and low temperature, on the destruction rate of amino acids when irradiated with Mars-like UV radiation. We measured the destruction rate of ~300 nm thick polycrystalline films of glycine deposited on silicon substrates, when irradiated with UV (190-325 nm) in vacuum (~10^{-7} mbar), in a CO$_2$ atmosphere (~7 mbar), or when cooled to 210 K. The results show that the presence of a 7 mbar CO$_2$ atmosphere does not affect the destruction rate of glycine and that cooling the sample to 210 K (average Mars temperature) lowers the destruction rate by a factor of 7. A thin layer of water representative for martian conditions may have been accreted on the glycine film, but did not measurably influence the destruction rate. Our results form a basis for the understanding of more complex processes occurring on the martian surface, in the presence of regolith and other reactive agents. Low temperatures may enhance the stability of amino acids in certain cold habitable environments, which may be important in the context of the origin of life.

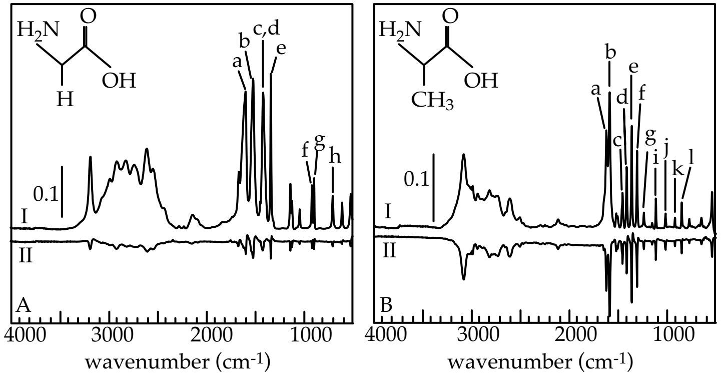

Fig. 6. The IR spectra of (A) solid glycine and (B) solid D-alanine in the range 4000-500 cm^{-1} measured with a resolution of 4 cm^{-1}. Two spectra are shown, (I) is recorded before irradiation with a deuterium discharge lamp, and (II) is obtained by subtracting the spectrum of the unirradiated compound from the spectrum recorded after ~50 hours of irradiation. Our lamp spectrum has a ~25 times lower integrated flux than the UV flux in equatorial regions on Mars in the same wavelength range. The vertical scale bars show the infrared absorption in absorption units.

We have investigated the intrinsic amino acid composition of two analogues of martian soil, JSC Mars-1 and Salten Skov in **Chapter 5**. A Mars simulation chamber has been built and used to expose samples of these analogues to temperature and lighting conditions similar to those found at low-latitudes on the martian surface. The effects of the simulated conditions have been examined using high performance liquid chromatography (HPLC). Exposure to energetic UV light in vacuum at room temperature appears to cause a modest increase in the concentration of certain amino acids within the materials. This is interpreted as resulting from the degradation of microorganisms. The irradiation of samples at low temperature (210 K) in the presence of a 7 mbar CO$_2$ atmosphere showed a modest decrease in the amino acid content of the soil samples It is probable that residual water, present in the chamber and introduced with the CO_2 atmosphere, was adsorbed on the mineral surfaces. Adsorbed water is key to the generation of reactive species on mineral grains, leading to the destruction of amino acids. This implication supports the idea that reactive chemical processes involving H_2O are at work within the martian soil. Furthermore, we have demonstrated that an analogue such as Mars-1, which is used as a spectral and physical match to a nominal average martian soil, is inappropriate for a life-science study in its raw state.

Chapter 6 focuses on the response of halophilic archaea to Mars-like conditions, such as low pressure, UV radiation and low temperatures. 'Halophiles' form a class of bacteria and archaea that live in environments with high salt concentrations, in the order of ten times higher than the salt concentration of ocean water. Mars is widely thought to have had liquid water present at its surface for geologically long periods. The progressive desiccation of the surface has likely led to an increase in the salt content of remaining bodies of water. If life had developed on Mars, then some of the mechanisms evolved in terrestrial halophilic bacteria to cope with high salt content may have been shared by martian organisms. We have exposed samples of the halophilic archaea *Natronorubrum* sp. strain HG-1 to conditions of UV radiation that are similar to those of the present-day martian environment. Furthermore, the effects of low temperatures and low pressure have been investigated. The results, obtained by monitoring growth curves by both optical and cell-counting methods, indicate that the present UV radiation at the surface of Mars is a significant hazard for this organism. Exposure of the cells to high vacuum inactivates ~50 % of the cells. Freezing to -20 °C and -80 °C kills ~80 % of the cells. When desiccated and embedded in a salt crust cells are somewhat more resistant to UV radiation than when they are suspended in an aqueous solution. The cell inactivation by UV radiation is wavelength dependent. Exposure to UV-A (longward of 300 nm) has no effect on the cell viability. Comparing irradiation using UV-B (250-300nm) to irradiation using UV-C (195-250 nm) indicates that UV-C is the most lethal to *Nr.* strain HG-1. Exposure to UV-B for a duration equivalent to ~80 hours of noontime equatorial illumination on the surface of Mars inactivated the proliferating capabilities of more than 95 % of the cells. From these experiments it can be concluded that *Nr.* strain HG-1 would not be a good model organism to survive on the surface of Mars, even when embedded in salt crystals.

Table 2. Chronology of Mars Exploration ‡

Mission name	**Launch data**	**Goal**
Marsnik 1 (Mars 1960A)	10 October 1960	Attempted mars fly by (launch failure)
Marsnik 2 (Mars 1960B)	14 October 1960	Attempted mars flyby (launch failure)
Sputnik 22	24 October 1962	Attempted mars flyby
Mars 1	1 November 1962	Mars flyby (contact lost)
Sputnik 24	4 November 1962	Attempted mars lander
Mariner 3	5 November 1964	Attempted mars flyby
Mariner 4	28 November 1964	Mars flyby
Zond 2	30 November 1964	Mars flyby (contact lost)
Zond 3	18 July 1965	Lunar flyby, mars test vehicle
Mariner 6	25 February 1969	Mars flyby
Mariner 7	27 March 1969	Mars flyby
Mars 1969A	27 March 1969	Attempted mars orbiter (launch failure)
Mars 1969B	2 April 1969	Attempted mars orbiter (launch failure)
Mariner 8	8 May 1971	Attempted mars orbiter (launch failure)
Cosmos 419	10 May 1971	Attempted mars orbiter/lander
Mars 2	19 May 1971	Mars orbiter/ attempted lander
Mars 3	28 May 1971	Mars orbiter/ lander
Mariner 9	30 May 1971	Mars orbiter (partner mission with Mariner 8)
Mars 4	21 July 1973	Mars flyby (attempted mars orbiter)

Mission name	**Launch data**	**Goal**
Mars 5	25 July 1973	Mars orbiter
Mars 6	5 August 1973	Mars lander (contact lost)
Mars 7	9 August 1973	Mars flyby (attempted mars lander)
Viking 1	20 August 1975	Mars orbiter and lander
Viking 2	9 September 1975	Mars orbiter and lander
Phobos 1	7 July 1988	Attempted mars orbiter and Phobos lander
Phobos 2	12 July 1988	Mars orbiter and attempted Phobos lander
Mars Observer	25 September 1992	Attempted mars orbiter (contact lost)
Mars Global Surveyor	7 November 1996	Mars orbiter
Mars 96	16 November 1996	Attempted mars orbiter/landers
Mars Pathfinder	4 December 1996	Mars lander and rover
Nozomi (Planet B)	3 July 1998	Mars orbiter
Mars Climate Orbiter	11 December 1998	Attempted mars orbiter
Mars Polar Lander	3 January 1999	Attempted mars lander
Deep Space 2 (DS2)	3 January 1999	Attempted mars penetrators
2001 Mars Odyssey	7 April 2001	Mars orbiter
Mars Express / Beagle 2	2 June 2003	Mars orbiter and attempted lander
Spirit (MER A)	10 June 2003	Mars rover
Opportunity (MER B)	7 July 2003	Mars rover

[‡] http://nssdc.gsfc.nasa.gov/planetary/factsheet/marsfact.html