Planetary and Space Science 58 (2010) 1617–1624

Contents lists available at ScienceDirect

Planetary and Space Science

journal homepage: www.elsevier.com/locate/pss

UVolution, a photochemistry experiment in low earth orbit: Investigation of the photostability of carbonates exposed to martian-like UV radiation conditions

Fabien Stalport [a,b,*], Yuan Yong Guan [a], Noblet Audrey [a], Patrice Coll [a], Cyril Szopa [c], Frédérique Macari [a], Alain Person [d], Didier Chaput [e], François Raulin [a], Hervé Cottin [a]

[a] Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), UMR 7583 CNRS, Universities of Paris 7 and Paris 12, C.M.C., 61 Avenue du Général de Gaulle 94010 Créteil Cedex, France
[b] NASA/Goddard Space Flight Center (GSFC), Code 699, 8800 Greenbelt Rd., Greenbelt, MD 20771, USA
[c] UPMC Univ. Paris 06; Université Versailles St-Quentin; CNRS/INSU, LATMOS-IPSL, 4 place Jussieu 75005 Paris Cedex, France
[d] Laboratoire de Biominéralisations et Paléoenvironnements, University Pierre et Marie Curie-Paris VI, Paris, France
[e] Centre National d'Etudes Spatiales, 18 avenue Edouard Belin 31401 Toulouse Cedex 9 France

ARTICLE INFO

Article history:
Received 18 May 2010
Received in revised form
20 July 2010
Accepted 2 August 2010
Available online 12 August 2010

Keywords:
Mars
Astrobiology
UV radiation
Carbonates
Biominerals
Low Earth orbit

ABSTRACT

The detection and identification of carbonates on Mars are of prime importance to establish the evolution of its atmosphere, correlated to the history of the liquid water, or even to determine the existence of a possible ancient biological activity. Till date, no large deposits of carbonates have been found. In fact, their detection is specific to local areas and in very low amounts. The absence of such deposits is commonly attributed to the harsh environmental conditions at the surface of Mars. Additionally, the presence of UV radiation has been proposed to explain their photodecomposition and hence their absence. However, contradictory results from laboratory experiments mimicking Mars' surface UV radiation did not resolve the behaviour of carbonates in such an environment, which is why we exposed, in low Earth orbit and in laboratory experiments, both abiotic and biotic calcium carbonates to UV radiation of wavelength above 200 nm, the same spectral distribution as the one reaching the surface of Mars. For low Earth orbit (LEO) exposure, this was done for the UVolution experiment on board the BIOPAN ESA module, which was set outside a Russian Foton automated capsule, and exposed to space conditions for 12 days in September 2007. The targeted carbonates are biominerals and abiotic samples. Our laboratory results mainly show that the exposed carbonates appear to be stable to UV radiation if directly exposed to it. The LEO experiment results tend to the same conclusion, but the integrated exposition time to Solar UV during the experiment is not sufficient to be conclusive. However, the stability of the biominerals derived from the laboratory experiment could strengthen the interest to explore deeper their potential as life records at Mars. Hence, they should be considered as primary targets for *in situ* analyses during future missions.

1. Introduction

Several geochemical and geomorphologic evidences indicate that the martian environment was moister during the first 500–700 millions of years after the formation of the planet (Squyres et al., 2004; Poulet et al., 2005; Bibring et al., 2006). The presence of perennial liquid water would have been favoured by greenhouse gases in large amounts in the atmosphere (Kasting et al., 1992; Brown and Kasting, 1993; Forget and Pierrehumbert, 1997; Justh and Kasting, 2002; Kasting, 2002). Among these gases, CO_2 should have been the most important one, and it could have played an important role in warming up the surface of Mars. Besides, the interaction of liquid water and gaseous CO_2 in the atmosphere can generate carbonates. Hence, the formation of carbonates could have occurred on Mars. Their detection is of paramount importance. First, they could aid in understanding the evolution of the martian atmosphere, and by extension the story of the liquid water, since the formation of carbonate deposits has been proposed to explain part of the gradual loss of the martian atmosphere leading to its known current dry and cold environment. Second, they could provide traces of a potential past biological activity: on Earth, the carbonates are important biominerals which are produced by two distinct processes:

---

[*] Corresponding author at: NASA/Goddard Space Flight Center (GSFC), Code 699, 8800 Greenbelt Rd., Greenbelt, MD 20771, USA. Tel.: +1 301 614 5112.
E-mail addresses: Fabien.Stalport@lisa.univ-paris12.fr, fabien@umbc.edu (F. Stalport).

0032-0633/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.pss.2010.08.005

"biologically controlled" and "biologically induced" mineralization in eukaryotes and prokaryotes, respectively (Mann, 2001; Weiner and Dove, 2003). Such processes could have taken place on Mars and biogenic organic material could have been trapped in carbonate layers. It is also important to note that the carbonates can be fossil records capable of surviving several billions of years (Allwood et al., 2006).

The thermal infrared spectra of the martian dust indicated the presence of low concentrations (~2 to 5 wt%) of carbonates at the martian surface, specifically dominated by magnesite ($MgCO_3$), but without a clear indication of a concentrated source (Bandfield et al., 2003). Similar observations have been obtained with the thermal and evolved gas analyzer of the Phoenix Lander (3–5% calcium carbonate in the arctic soil) (Boynton et al., 2009). The Mars Reconnaissance Orbiter has revealed for the first time a regional rock layer with near-infrared spectral characteristics that are consistent with the presence of magnesium carbonate in the Nili Fossae region located at 22°N, 75°E with an estimated age of 3.5 Ga or more (Ehlmann et al., 2008). Furthermore, recently outcrops rich in Mg–Fe carbonate (16–34 wt%) have been identified by the miniature thermal emission spectrometer on board the Spirit in the Columbia Hills of Gusev crater (Morris et al., 2010).

Nevertheless, the detection of carbonates is limited to very specific to local areas and reveals only trace amounts: no large deposit has been observed, like on Earth. Several assumptions have been investigated to explain the lack of large deposits of carbonates: (i) the formation of such deposits could have been inhibited (Bullock and Moore, 2007), (ii) if carbonates deposits ever were present, they could have been destroyed by acidic aqueous activity (Fairén et al., 2004), (iii) they could be present on Mars, but obscured by younger rock materials, (iv) they could be decomposed by UV radiation reaching the surface of Mars (Mukhin et al., 1996). The conclusion of an acidic environment does not consider that multiple aqueous environments could be present on the planet at the same time (Bandfield, 2008). The detection of carbonates themselves, and the preliminary data recovered from the Wet Chemistry Labs on Phoenix (Kounaves et al., 2009), indicate that some aqueous environments have been compatible with the production of carbonates. If the carbonates are obscured by younger rock materials, *in situ* exploration missions are required to detect them in samples collected in the subsurface. Finally, the photodecomposition of carbonate deposits also presents an interesting explanation: the carbonate deposits, recently exposed to UV radiation by wind erosion processes of younger materials, possibly could be quickly destroyed (the carbonates detected by the MRO and MER missions could have been exposed to radiation only recently).

Mukhin et al. (1996) reported that photodecomposition of carbonates can occur on Mars, based on experimental simulations in which natural pure calcite crystal decomposed when exposed to UV light under vacuum. While they concluded that the rate of carbonate degradation is high enough to explain the apparent absence of these compounds at Mars' surface, other laboratory experiments showed that the decomposition of pure calcite does not take place in the presence of a martian-like atmosphere (Quinn et al., 2006) and that carbonates can form under conditions similar to those on Mars even with UV light present (Booth and Kieffer, 1978).

In an attempt to understand these contradictory results, we investigated the evolution of natural carbonates (calcite and aragonite) under martian-like UV radiation by conducting a series of laboratory and low Earth orbit experiments. Indeed, the UV radiation experiments in a laboratory are a good support for such studies, especially because it is possible to control environmental parameters such as the flux and the spectrum of UV sources, or the samples temperature. Nevertheless, no available UV source is capable of perfectly mimicking the UV flux and spectrum reaching the martian surface. In order to complete these studies and validate results obtained with laboratory experiments, it is important to compare them with experiments conducted with an adequate UV spectrum. Therefore, we have exposed carbonate samples to the solar UV radiation in low Earth orbit, where the UV spectrum reaching our samples is similar to that reaching the surface of Mars in the 200–400 nm wavelength range (Patel et al., 2002).

This article describes the results obtained from the study of the evolution of carbonates exposed to a martian-like UV source in laboratory with the MOMIE experiment (Stalport et al., 2008, 2009), and those obtained from the UVolution experiment that flew in low Earth orbit (Cottin et al., 2008). This low Earth orbit experiment was developed by the Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), and it was supported both by the European and French Space Agencies (ESA and CNES). This experiment has also been supported scientifically by the Laboratoire des ATmosphères Milieux Observations Spatiales (LATMOS). The UVolution experiment was part of the Biopan-6 payload set outside the Foton-M3 Russian automated capsule that has orbited Earth in September 2007 for 12 days, at roughly 300 km altitude. Biopan is an ESA exposure facility, which enables a direct exposure of various samples to space conditions (Demets et al., 2005). The UVolution experiment consists of exposing mineral and organic materials to solar UV for the study of comets, meteorites, Mars, and Titan. The results concerning organic material related to Mars have been already published in Stalport et al. (2010). This article focuses on the results of the evolution of mineral samples of interest for Mars, and on their implication for the survival of carbonates in Mars' surface environment.

2. Material and method

Four samples have been selected for the UVolution mission and the MOMIE experiment: two abiotic crystals and two biominerals (presented in Table 1). We have also chosen to study biominerals because Mars would have been particularly hospitable to the emergence of life, in a period when life arose on the Earth for these following reasons: (i) the presence of long-standing liquid water (Klingelhöfer et al., 2004; Poulet et al., 2005; Bibring et al., 2006; Treiman, 2008), (ii) at least one source, i.e. the interplanetary medium, of organic materials of prebiotic interest (Cottin et al., 1999; Botta and Bada, 2002; Pizzarello et al., 2006; Glavin et al., 2008), and (iii) an atmosphere sufficiently dense for liquid water to be stable at the surface. We then assumed that fossils of a potential past biological activity could have been more efficiently preserved in the form of inorganic materials like biominerals. As it is possible to discriminate biotic from abiotic carbonates with space instrumentation (Cabane et al., 2004; Stalport et al., 2005, 2007), we then investigated the impact of UV radiation on the preservation of the biological signature of the biominerals. An energy deposit (thermal treatment in Orofino et al., 2007, and maybe from UV radiation in this experiment) could modify the mineral structure of the biomineral, especially the transformation of biotic aragonite in a kind of calcite (Orofino et al., 2007).

As the number of samples was limited for the UVolution mission (8 exposure cells available for Mars-related carbonate samples), focus was given on calcium carbonates, aragonite, and calcite. We focused our study on calcium carbonates produced by "biologically induced" mineralization (Table 1) because prokaryotic organisms are the most primitive life forms known on Earth. As the martian surface environmental conditions were probably

Table 1
Description of the samples and the corresponding relative variation of the infrared spectra area, compared before and after the flight in orbit.

Sample	Description	Variation area ($4000–2080\,cm^{-1}$)
Abiotic calcite Iceland spar, Iceland	Sample A exposed	+0.2%
	Sample B exposed	+1.5%
	Sample C not exposed	−0.2%
	Sample D not exposed	+2.1%
	Sample E ground	−0.1%
	Sample F ground	−0.2%
	Sample G ground	+0.4%
	Sample H ground	+1.7%
Biotic calcite stromatolite, Bolivia (Coipassa)	Sample A exposed	+1.5%
	Sample B exposed	−0.6%
	Sample C not exposed	−0.8%
	Sample D not exposed	+1.8%
	Sample E ground	−0.3%
	Sample F ground	N/A
	Sample G ground	N/A
	Sample H ground	N/A
Abiotic aragonite, aragonite crystal, Morocco	Sample A exposed	−4.4%
	Sample B exposed	+4.0%
	Sample C not exposed	+3.1%
	Sample D not exposed	−0.7%
	Sample E ground	−5.1%
	Sample F ground	+3.8%
	Sample G ground	−1.5%
	Sample H ground	−1.3%
Biotic aragonite microbialite, France	Sample A exposed	+4.7%
	Sample B exposed	+0.3%
	Sample C Not exposed	+4.9%
	Sample D not exposed	N/A
	Sample E ground	+2.1%
	Sample F ground	+4.5%
	Sample G ground	+3.7%
	Sample H ground	+4.0%

favourable for the emergence and evolution of life for only a short period (estimated to be only several hundred millions of years), prokaryotes are therefore the organisms the most likely to have ever emerged and evolved on Mars.

For the UVolution space experiment, the carbonates were deposited inside open exposition cells (more details in Cottin et al., 2008). The cells devoted to the "martian" samples are composed of a cylindrical aluminium body and a quartz window (1 mm thick, 9 mm diameter) on which our samples are deposited. Quartz windows filter UV radiation under 200 nm wavelengths, and they are transparent to higher wavelengths, simulating the UV spectrum at the surface of Mars. Indeed, UV photons reaching the Mars surface would be in the 190–400 nm wavelength range (Kuhn and Atreya, 1979; Cockell et al., 2000; Patel et al., 2002), whereas the wavelength range of the UV solar spectrum is much wider (10–400 nm). The carbonates were directly deposited on the surface of the windows to measure the photolysis rate or the UV resistance of the targeted sample.

The carbonate samples were sieved (granulometry selected under 40 μm diameter) and dispersed by mechanical agitation as a powder in ethanol to prepare a suspension. Each solution was then deposited on the quartz window surface and heated to 50 °C to evaporate the ethanol. Hence, the carbonate films were obtained by evaporation and the thickness of each sample is about several hundred micrometers (determined by interferometric techniques).

For each sample, four deposits were prepared for the flight. They were kept in an inert atmosphere before being sent into orbit. Among them, two deposits were exposed to the solar radiation, and the two others were kept in the dark below the exposed ones: these are space dark controls (Fig. 1). Four samples of each kind were also prepared to be kept in the laboratory as ground controls. They were stored under vacuum under a controlled temperature in the laboratory.

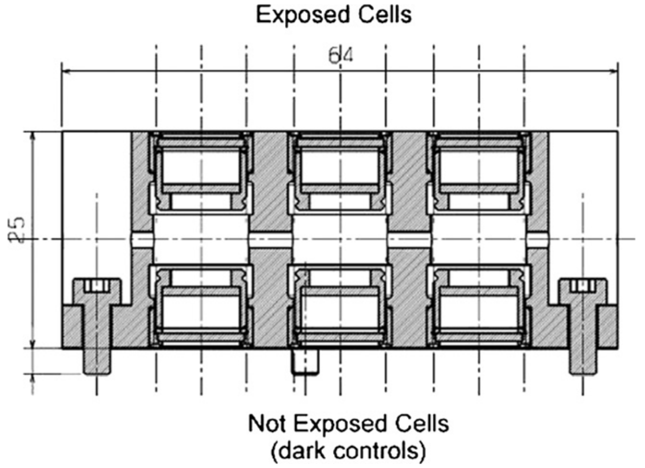

Fig. 1. Schematic of the arrangement of the cells. On the top, the cells are directly exposed to the solar UV radiation whereas on the bottom, the cells are kept in the dark.

The carbonate evolution was measured by Fourier transform infrared spectroscopy (FTIR) (Perkin Elmer—BXII spectrometer resolution: $4\,cm^{-1}$; number of scans: 8). We also compared images of the deposits before and after the flight with a binocular magnifying glass (zoom ×10) to evaluate a potential qualitative evolution.

The cells were directly inserted in the measurement compartment of the instrument. The infrared spectrum of each sample was measured by transmission through the quartz window. A background measurement was performed with an empty cell. The acquisition range was set between 4000 and $2080\,cm^{-1}$ due to the transmission properties of the quartz window in the infrared wavelength range. An important part of the infrared range was then inaccessible. It is important to keep in mind that we have no *in situ* measurements during the flight. We then had two transmission spectra for each sample: one was recorded before the flight, and the other one, after the flight. The areas of the corresponding infrared bands were then compared in order to determine a possible modification of the samples properties (total absorbance area in the $3100–2300\,cm^{-1}$ range), and to calculate their photolysis rate when it is applicable. These two analyses are separated by 30 days, from the preparation of the sample, to its return to the laboratory for analysis after the flight.

Photolysis of the targeted carbonates was also implemented in the laboratory. We have developed an experiment (MOMIE, described in Stalport et al., 2008, 2009) to study the evolution of organics and minerals, especially biominerals, under Mars' surface environmental conditions, mainly including radiation and oxidants. The first step of this project is to reproduce as closely as possible the UV radiation reaching Mars' surface, and to submit various materials of astrobiological interest to these radiation. With this aim, a UV source releasing photons in the 190–400 nm wavelength range was used. The UV flux of the source in the range 190–290 nm wavelength range (wavelength range supposedly reaching the surface of Mars but not the surface of the Earth) is $11 \pm 3\,W/m^2$ ($4.0 \pm 0.3\,W/m^2$ at the surface of Mars (Cockell et al., 2000; Patel et al., 2002)), and it is focused on a surface of $0.8\,cm^2$ (the surface of a deposit). The UV flux and spectrum have been provided by the LOT-ORIEL company, and they were measured with a Jobin Yvon monochromator. For this experiment, the carbonate films were also produced with the same protocol as previously described, but MgF_2 windows were used because of the transmission properties of MgF_2 in the infrared domain (down to 1000 cm^{-1}). Indeed, in this case, no filtering of the UV radiation shorter than 200 nm was required because the emission spectrum of the laboratory lamp begins at approximately 190 nm; hence, the lamp spectrum directly mimics the radiation supposedly reaching Mars' surface. The evolution of the samples was also measured by transmission infrared spectroscopy following the same procedure as previously described.

3. Results

3.1. Low earth orbit results

The photolysis of an A molecule by UV radiation into new products can be described by the following equation:

$$A \xrightarrow{h\upsilon} \text{products} \tag{1}$$

This equation can then be mathematically described following the equation

$$\frac{d[A]}{dt} = -J[A] \tag{2}$$

If the kinetics of photolysis is of first order (meaning the hypothesis of an optically thin sample in the UV domain), with [A] the abundance of A molecule, the irradiation time and J the photolysis rate ($[\text{time}]^{-1}$), then this equation can be resolved following the equation

$$\frac{Ln[A]_t}{Ln[A]_0} = -Jt \tag{3}$$

Then, by comparing results obtained for different film thicknesses (i.e. for different time of irradiation) of the same molecule (i.e. different [A]) and the relevant areas of the infrared spectra, we obtained a linear correlation between them. We can then determine the abundance of a molecule before and after the exposure. Regarding the Foton capsule orbiting the Earth, freely rotating around its longitudinal axis, its samples are not continuously exposed to the Sun. The integrated photolysis time during the experiment in orbit (t) has been estimated to 29 solar constant hours with an uncertainty of 15% in the 220–280 nm range. The exposure time is derived from on board sensors provided by ESA, cross-correlated with an orbital calculation provided by the RedShift Company (St Niklaas, Belgium). This corresponds to an amount of UV-C equal to 1.2 ± 0.2 days with Sun at zenith.

The results of direct exposure in low Earth orbit are shown in Table 1. No significant results can be derived from them. In fact, the area variations of both exposed and non-exposed samples are quite similar before and after the exposition in low Earth orbit. Table 1 summarizes the area variation of the IR spectra collected before and after the flight. Nevertheless, major constraints put into perspective these results: positive and negative variations are measured for exposed, not exposed, and ground samples. By observing the evolution of the infrared bands' area for the unexposed and ground samples (not exposed to UV radiations), an uncertainty of ± 5% can be estimated. This large uncertainty is due to the fact that we cannot compare the most intense bands of both aragonite and calcite infrared spectra. These intense bands can only be observed for wavenumbers below 2000 cm^{-1} and because of the properties of the quartz windows, this wavenumber range is not accessible; only weak absorption features of the mineral (absorbance <1) can be measured in the 4000–2080 cm^{-1} range, associated to quite significant uncertainties due to the instrumental noise level.

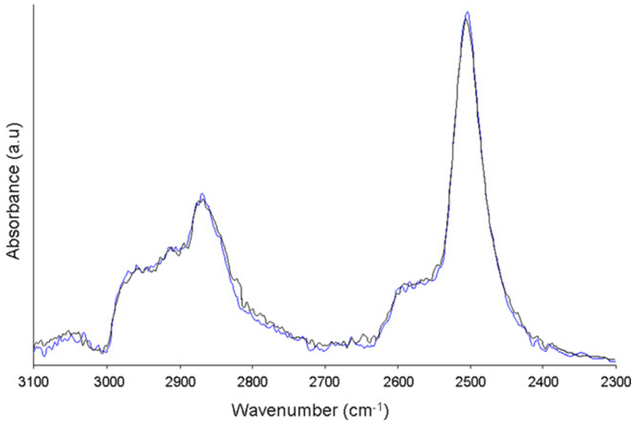

Fig. 2. IR spectra of biotic calcite measured before (black) and after (blue) the flight in orbit in the 3100–2300 cm^{-1} wavelength range with a 4 cm^{-1} resolution. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Hence, any variations of the area of infrared bands of the exposed samples are included within the variation range of the dark control and ground samples. Nevertheless, the carbonates seem to not have been photodegraded by UV radiation. Figs. 2 and 3 show the infrared spectra of a cell containing, respectively, biotic calcite and aragonite samples before and after exposure in space. Both spectra are quite similar and indicate that the exposed carbonates remained stable during the experiment. We observed the same results with the abiotic calcite and aragonite samples. We also calculated the upper limit of the photodegradation rate carbonate samples in low orbit in the 200–290 nm range from LEO experiments regarding the uncertainty. We estimated that this upper limit could correspond to a photodegradation rate of the carbonate samples of about 0.02 molecules/photon.

The comparison of pictures of the deposits recorded before and after the flight, with a binocular magnifying glass, did not show any pronounced macroscopic alteration. For example Figs. 4 and 5, respectively, present the comparison of pictures of the biotic calcite and aragonite samples.

3.2. Laboratory results

The durations of irradiation in the laboratory are longer than for the experiment in orbit (300 h of direct exposure for calcite samples and 200 h for aragonite samples). Both integrated fluxes for the sun at the top of the terrestrial atmosphere and the UV source are similar: 10 W/m^2 for the former (Thuillier et al., 2004) and 11 ± 3 W/m^2 for the latter. We focused on the 200–290 range because the UV radiations are filtered by the terrestrial atmosphere below 290 nm and the carbonate deposits at the surface of the Earth are stable.

The area variations of the carbonates after several hours of irradiation are null with an uncertainty of ± 0.03%. These variations are measured this time on the most intense absorption bands, in the 1000–4000 cm^{-1} wavenumber range. We especially focused on the major peaks of calcite (1391 cm^{-1}) and aragonite (1448 cm^{-1}) resulting in a higher signal to noise ratio than for the samples exposed in space.

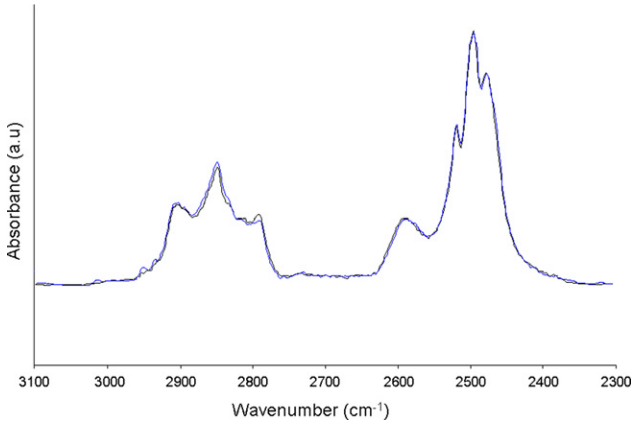

Fig. 3. IR spectra of biotic aragonite measured before (black) and after (blue) the flight in orbit in the 3100–2300 cm^{-1} wavelength range with a 4 cm^{-1} resolution. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

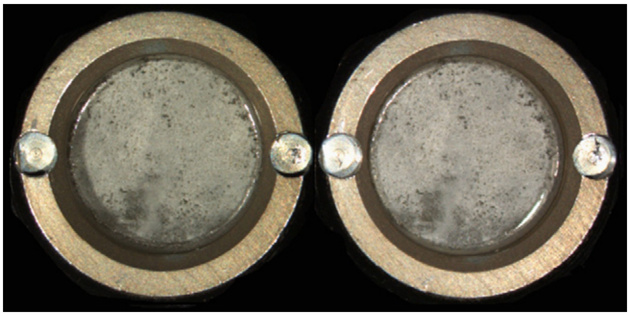

Fig. 4. Images of a deposit of biotic calcite before (left) and after (right) flight (zoom ×10).

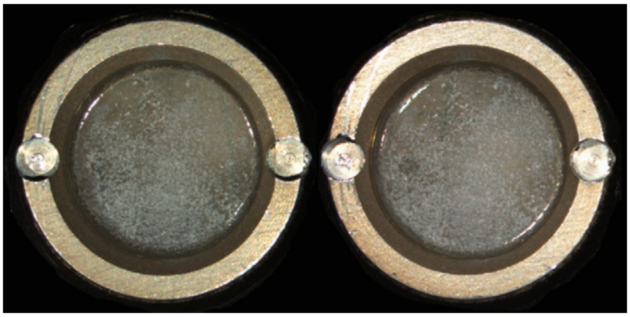

Fig. 5. Images of a deposit of biotic aragonite before (left) and after (right) flight (zoom ×10).

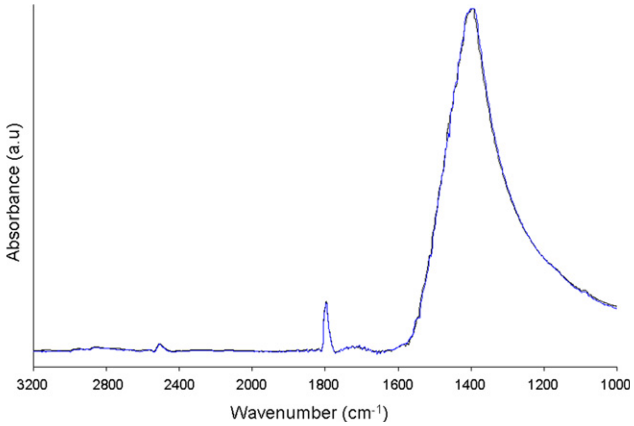

Fig. 6. IR spectra of biotic calcite measured before (black) and after (blue) the laboratory irradiation experiments in the 3200–1000 cm^{-1} wavelength range with a 4 cm^{-1} resolution. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

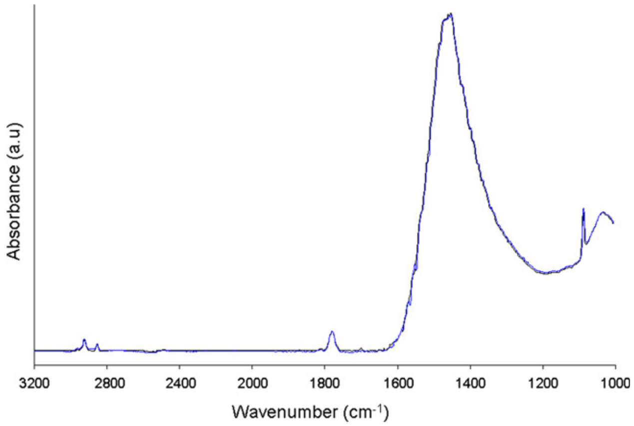

Fig. 7. IR spectra of biotic aragonite measured before (black) and after (blue) the laboratory irradiation experiments in the 3200–1000 cm^{-1} wavelength range with a 4 cm^{-1} resolution. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Since the area variation of the infrared spectra was not significant, we can conclude that abiotic calcite, biotic calcite, abiotic aragonite, and biotic aragonite are not photolysed. Figs. 6 and 7, respectively, show spectra of the biotic calcite and aragonite samples before and after irradiation. No new spectral feature or change in the shape of the infrared spectra has been observed. For example, we did not observe the transition from aragonite samples to the formation of any kind of calcite. Nevertheless, we also calculated the upper limit of the photodegradation rate carbonate samples in laboratory experiments in the 200–290 nm the laboratory uncertainty. We estimated that this upper limit could correspond to a photodegradation rate of the carbonate samples of about 7×10^{-6} molecules/photon on Mars.

4. Discussion

This low Earth orbit experiment is the first step for the study of the evolution of minerals and biominerals under martian-like conditions. The preliminary results are not conclusive because the wavenumber range studied is not adequate and the uncertainty remains too high. The interpretation of these data then appears more qualitative than quantitative. The samples do not seem to have been significantly affected by UV radiation in low Earth orbit. Conversely, according to the uncertainty of ±5%, the degradation rate could reach an upper limit of 0.02 molecules/photon approximately. This would mean that the rate of carbonate decomposition would exceed those obtained by Mukhin et al. (1996) (between 4×10^{-5} and 2×10^{-6} molecules/photon) and by Quinn et al. (2006) (lower limit 3.5×10^{-8} molecules/photon). Quinn et al. (2006) considered that their value could not explain the lack of carbonates on the surface of Mars. Conversely, Mukhin et al. (1996) concluded that for the surface of Mars, this rate would be approximately 10^6 and 10^8 molecules/

cm^2/s, assuming a carbonate abundance in the martian soil in the 0.01% and 1% range approximately, and this could explain the lack of carbonate deposits. From our upper limit rate, we can extrapolate the destruction of a layer of one hundred meters of carbonates for 220 000 years, which could then explain the lack of large deposits of carbonate on the surface of Mars.

We also performed a laboratory experiment in order to complete low Earth orbit data and found the behaviour of carbonates under UV radiation to be more significant. Our results show that the direct exposure to UV radiation, in laboratory conditions, does not lead to their photodissociation, contrary to what was shown by Mukhin et al. (1996). We calculated an upper limit that could correspond to a photodegradation rate of the carbonate samples of about 7×10^{-6} molecules/photon. This value is in the range of those from the article of Mukhin et al. (1996). Nevertheless, we estimated that the comparison is not pertinent and that the data provided by Mukhin et al. (1996) could be debated. Crucial information concerning the experimental device or the UV source (spectrum and flux) is missing. Finally, the release of CO_2 (from the photodegradation of calcite) in their vacuum chamber, due to a short period of UV irradiation of the surface of their calcite sample, could be easily interpreted as desorption effects of atmospheric CO_2 molecules from the inside surface of the vacuum chamber itself and not from a potential photodegradation of calcite sample. Nevertheless from our upper limit rate from laboratory data, we can extrapolate the destruction of a layer of one hundred meters of carbonates for about 630 million years. This result could then explain the lack of large deposits of carbonate on the surface of Mars.

Conversely, the laboratory results we obtained confirm the laboratory results of Booth and Kieffer (1978) and more recently, those of Quinn et al. (2006), even if the experimental conditions and data acquisitions are quite different. They are also in accordance with the observations performed by the Mars Reconnaissance Orbiter (Ehlmann et al., 2008; Morris et al., 2010), and *in situ* analyses performed by the Phoenix lander (Boynton et al., 2009) that showed the presence of carbonates on Mars. Quinn et al. (2006) found no experimental evidence of the UV photodecomposition of calcium carbonate in a simulated martian atmosphere. In fact, they were unable to detect carbonate decomposition in the limit of their experimental system ($\sim3.10^{-8}$ molecules/photon). However, they indicated that if calcium carbonates would be stable in a CO_2 atmosphere, they could decompose under vacuum (Mukhin et al., 1996), and in vacuum, the decomposition of $CaCO_3$ may occur because of the photodetachment and photodissociation of CO_3^- radical defects generated by UV light (Bartoll et al., 2000). In a CO_2 atmosphere, the decomposition of $CaCO_3$ would be inhibited by the reformation of the UV-generated CO_3^- by adsorbed CO_2 and surface O^- radicals (Quinn et al., 2006). In our experiments, both low Earth orbit and laboratory experiments are performed under vacuum: the UVolution cells are opened and any residual gas is vented to space. An active pumping system also maintains a low pressure in the MOMIE experiment (more details in Stalport et al., 2009). The calcium carbonates seem to be stable in the Mars-like surface conditions of our experiments, even in the absence of a CO_2 atmosphere. Hence, based on our laboratory experimental results, we assume that the photodissociation of carbonates does not occur on Mars, and the UV radiation reaching the surface is not responsible for the absence of large deposits of carbonates. A review of all the discussed results is presented in Table 2.

Table 2
Review of the different results for the exposition of calcite to UV radiation. The flux of UV source for Mukhin et al. (1996) cannot be estimated because no information has been provided.

	Irradiation time (h)	Flux 200–290 (W/m^2)	Upper limit (molecule/s)
Mukhin et al. (1996)	4	N/A	4×10^{-5}– 2×10^{-6}
Quinn et al. (2006)	70	11.5	3.5×10^{-8}
Low Earth orbit	29 ± 4	10	0.02
MOMIE experiment	300	11 ± 3	7×10^{-6}

The second objective of these experiments was to investigate the potential influence of UV radiation on the signature of biotic carbonates. If we assume that life emerged on Mars, fossil records of its activity could have survived for several billions years, till date (Morrison, 2001). The most common materials known to be produced by living organisms are organic molecules, and they are considered priority targets for detecting a potential martian life (McKay, 2004). However, if we exclude methane detected in the atmosphere by remote sensing (Formisano et al., 2004; Krasnopolsky et al., 2004), no organic molecule has ever been detected on the surface of Mars with *in situ* analysis (Biemann et al., 1977). Furthermore, even if future space probes do attempt to search for organic molecules on the martian surface, organics are expected to be present at very low levels on Mars because they could be destroyed by the harsh surface conditions (Cockell et al., 2000; Patel et al., 2002; Dartnell et al., 2007; Wu, 2007; Lefèvre and Forget, 2009; Stalport et al., 2009, 2010), making their detection challenging. The carbonates are important biominerals that are produced by eukaryotes and prokaryotes. They are worth investigating strategic targets as previous studies showed it is possible to discriminate biominerals from their abiotic counterparts by *in situ* analyses on Mars like thermal analysis (Stalport et al., 2005, 2007). Orofino et al. (2007, 2009) showed that heat treatments of biotic and abiotic aragonite samples lead to their transformation into a kind of calcite (Orofino et al., 2007, 2009). They pointed out that after an energy deposit like thermal processing (UV radiation could be such an energy deposit), it is possible to distinguish, by means of infrared spectroscopy, biotic carbonate samples from their abiotic counterparts. However, an energy deposit like thermal processing erases the mineralogical signature of aragonite by transforming into calcite, which is why we also focused on the potential stability of biominerals under UV radiation. As we did not measure any evolution of the biotic mineral under UV radiation, especially with the laboratory experiments, we conclude that the record of their biological origin over the ages in the harsh martian environment could then be preserved. Hence, this physical signature can potentially be used to search for evidence of life on Mars in future missions, using any method capable to detect it, such as the thermal analysis of the decomposition of carbonates (Stalport et al., 2005, 2007).

5. Conclusion

The UVolution low Earth orbit experiment consists of exposing compounds (organic molecules and minerals) of astrobiological interest to the solar UV photons. Some of the samples were selected to study the behaviour and stability of the abiotic and biotic calcium carbonates which could be present on Mars. Measurements have shown that a clear conclusion is not possible based on this first low Earth orbit experiment. According to the wavenumber range studied and the uncertainty, both interpretations could be validated: under UV radiation, the carbonates samples could be either stable or decomposed. On the other hand, our laboratory experiments concluded that the targeted carbonates are radiotolerant; therefore, the photodissociation of carbonates should not occur on Mars, and the UV radiation reaching the surface should not be responsible for the absence of large deposits of carbonates. Because the investigated biominerals were shown to remain stable after the UV irradiation, their stability is crucial to their preservation as biotic signatures on the surface of Mars. As technical tools are able to discriminate biominerals from their abiotic minerals, it appears important to explore more deeply the potential of the biological signature of the biominerals, especially the carbonates.

As it is still difficult to provide a definitive status about the evolution of carbonates on Mars, we continue to argue that such space experiments are important and must be supported by laboratory experiments because of the more efficient representativity of the martian-like UV conditions. Such space experiments could enable a better understanding about the history and evolution of carbonates, and also biocarbonates, in the environment of Mars, if their duration is long enough. Furthermore, new data about the photostability of martian-related compounds (carbonates included) should soon be available. Samples in quartz cells are among the samples accommodated in the PROCESS experiment, which is part of the EXPOSE-Eutef ESA exposure facility installed outside the Columbus module of the International Space Station since February 2008, samples which returned to Earth in September 2009 (Cottin et al., 2008). PROCESS is quite similar to UVolution (same kind of hardware and samples), except that a longer exposure time to solar UV radiation is expected (10–20 times more than during the Biopan-6 mission), enabling the acquisition of more accurate data on the studied samples.

Acknowledgements

This program has been selected by ESA in the frame of the AO Life and Physical Sciences and Applied Research Projects 2004. The authors would like to acknowledge the support of ESA (especially René Demets), CNES (especially Michel Viso for the human, financial, and technical supports), French Program for Planetology (PNP), COMAT aerospace (Toulouse, France), and Kayser Threde (Munchen, Germany). The authors also acknowledge Jennifer Stern and Amy Houghton for helpful comments.

References

Allwood, A.C., Walter, M.R., Kamber, B.S., Marshall, C.P., Burch, I.W., 2006. Stromatolite reef from the early Archaean era of Australia. Nature 441, 714–718.

Bandfield, J.L. 2008. A complex history of martian surface mineralogy and aqueous processes. Lunar and Planetary Institute Science Conference Abstracts, Vol. 39, p. 1741.

Bandfield, J.L., Glotch, T.D., Christensen, P.R., 2003. Spectroscopic identification of carbonate minerals in the Martian dust. Science 301, 1084–1087.

Bartoll, J., Stößer, R., Nofz, M., 2000. Generation and conversion of electronic defects in calcium carbonates by UV/vis light. Applied Radiation and Isotopes 52, 1099–1105.

Bibring, J.-P., Langevin, Y., Mustard, J.F., Poulet, F.A. ç.A.o., Arvidson, R., Gendrin, A., Gondet, B., Mangold, N., Pinet, P., Forget, F., 2006. Global mineralogical and aqueous mars history derived from OMEGA/Mars express data. Science 312, 400–404.

Biemann, K., Oro, J., Toulmin, P., Orgel, L.E., Nier, A.O., Anderson, D.M., Simmonds, P.G., Flory, D., Diaz, A.V., Rushneck, D.R., et al., 1977. The search for organic substances and inorganic volatile compounds in the surface of Mars. Journal of Geophysical Research 82, 4641–4658.

Booth, M.C., Kieffer, H.H., 1978. Carbonate formation in Marslike environments. Journal of Geophysical Research 83, 1809–1815.

Botta, O., Bada, J.L., 2002. Extraterrestrial organic compounds in meteorites. Surveys in Geophysics 23, 411–467.

Boynton, W.V., Ming, D.W., Sutter, B., Arvidson, R.E., Hoffman, J., Niles, P.B., Smith, P., Team, P.S., 2009. Evidence for calcium carbonate at the Phoenix landing site. Lunar and Planetary Institute Science Conference Abstracts, Vol. 40, p. 2434.

Brown, L.L., Kasting, J.F., 1993. A carbon dioxide/methane greenhouse atmosphere on early Mars. Workshop on Early Mars: How Warm and How Wet? (Part 1), Lunar and Planetary Institute, p. 3.

Bullock, M.A., Moore, J.M., 2007. Atmospheric conditions on early Mars and the missing layered carbonates. Geophysical Research Letters 34, 19201.

Cabane, M., Coll, P., Szopa, C., Israel, G., Raulin, F., Sternberg, R., Mahaffy, P., Person, A., Rodier, C., Navarro-Gonzalez, R., et al., 2004. Did life exist on Mars? Search for organic and inorganic signatures, one of the goals for "SAM" (sample analysis at Mars). Advances in Space Research 33, 2240–2245.

Cockell, C.S., Catling, D.C., Davis, W.L., Snook, K., Kepner, R.L., Lee, P., McKay, C.P., 2000. The ultraviolet environment of mars: biological implications past, present, and future. Icarus 146, 343–359.

Cottin, H., Coll, P., Coscia, D., Fray, N., Guan, Y.Y., Macari, F., Raulin, F., Rivron, C., Stalport, F., Szopa, C., et al., 2008. Heterogeneous solid/gas chemistry of organic compounds related to comets, meteorites, Titan, and Mars: laboratory and in lower Earth orbit experiments. Advances in Space Research 42, 2019–2035.

Cottin, H., Gazeau, M.C., Raulin, F., 1999. Cometary organic chemistry: a review from observations, numerical and experimental simulations. Planetary and Space Science 47, 1141–1162.

Dartnell, L.R., Desorgher, L., Ward, J.M., Coates, A.J., 2007. Modelling the surface and subsurface Martian radiation environment: implications for astrobiology. Geophysical Research Letters 34, 02207.

Demets, R., Schulte, W., Baglioni, P., 2005. The past, present and future of Biopan. Advances in Space Research, Space Life Sciences: Astrobiology: Steps toward Origin of Life and Titan before Cassini 36, 311–316.

Ehlmann, B.L., Mustard, J.F., Murchie, S.L., Poulet, F., Bishop, J.L., Brown, A.J., Calvin, W.M., Clark, R.N., Des Marais, D.J., Milliken, R.E., et al., 2008. Orbital identification of carbonate-bearing rocks on Mars. Science 322, 1828.

Fairén, A.G., Fernández-Remolar, D., Dohm, J.M., Baker, V.R., Amils, R., 2004. Inhibition of carbonate synthesis in acidic oceans on early Mars. Nature 431, 423–426.

Forget, F., Pierrehumbert, R.T., 1997. Warming early Mars with carbon dioxide clouds that scatter infrared radiation. Science 278, 1273.

Formisano, V., Atreya, S., Encrenaz, T., Ignatiev, N., Giuranna, M., 2004. Detection of methane in the atmosphere of Mars. Science 306, 1758–1761.

Glavin, D.P., Dworkin, J.P., Sandford, S.A., 2008. Detection of cometary amines in samples returned by Stardust. Meteoritics and Planetary Science 43, 399–413.

Justh, H.L., Kasting, J.F., 2002. Warming early Mars with CH_4. AGU Fall Meeting Abstracts, vol. 52, pp. 0371.

Kasting, J.F., 2002. Greenhouse models of early Mars climate. AGU Fall Meeting Abstracts, vol. 51, pp. 0345.

Kasting, J.F., Brown, L.L., Acord, J.M., Pollack, J.B., 1992. Was early Mars warmed by ammonia? Workshop on Martian Surface and Atmosphere Through Time, Lunar and Planetary Institute, pp. 84–85.

Klingelhöfer, G., Morris, R.V., Bernhardt, B., Schröder, C., Rodionov, D.S., de Souza, P.A., Yen, A., Gellert, R., Evlanov, E.N., Zubkov, B., et al., 2004. Jarosite and hematite at meridiani planum from opportunity's Mössbauer spectrometer. Science 306, 1740–1745.

Kounaves, S.P., Catling, D., Clark, B.C., Deflores, L., Gospodinova, K., Hecht, M.H., Kapit, J., Ming, D.W., Quinn, R.C., Team, P.S., 2009. Aqueous carbonate chemistry of the martian soil at the phoenix landing site. Journal 40, 2489.

Krasnopolsky, V.A., Maillard, J.P., Owen, T.C., 2004. Detection of methane in the martian atmosphere: evidence for life? Icarus 172 537–547.

Kuhn, W.R., Atreya, S.K., 1979. Solar radiation incident on the Martian surface. Journal of Molecular Evolution 14, 57–64.

Lefèvre, F., Forget, F., 2009. Observed variations of methane on Mars unexplained by known atmospheric chemistry and physics. Nature 460, 720–723.

Mann, S., 2001. Biomineralization: Principles and Concepts in Bioinorganic Materials Chemistry. Oxford University Press, New York.

McKay, C.P., 2004. What is life and how do we search for it in other worlds? PLoS Biology 2 1260–1263.

Morris, R.V., Ruff, S.W., Gellert, R., Ming, D.W., Arvidson, R.E., Clark, B.C., Golden, D.C., Siebach, K., Klingelhofer, G., Schroder, C., et al., 2010. Identification of carbonate-rich outcrops on Mars by the spirit rover. Science, 1189667.

Morrison, D., 2001. The NASA astrobiology program. Astrobiology 1, 3–13.

Mukhin, L.M., Koscheevi, A.P., Dikov, Y.P., Huth, J., Wänke, H., 1996. Experimental simulations of the photodecomposition of carbonates and sulphates on Mars. Nature 379, 141–143.

Orofino, V., Blanco, A., D'Elia, M., Fonti, S., Licchelli, D., 2009. Time-dependent degradation of biotic carbonates and the search for past life on Mars. Planetary and Space Science, Mars Analogues, Exploring Mars and its Earth Analogues 57, 632–639.

Orofino, V., Blanco, A., D'Elia, M., Licchelli, D., Fonti, S., 2007. Infrared transmission spectroscopy of carbonate samples of biotic origin relevant to Mars exobiological studies. Icarus 187, 457–463.

Patel, M.R., Zarnecki, J.C., Catling, D.C., 2002. Ultraviolet radiation on the surface of Mars and the Beagle 2 UV sensor. Planetary and Space Science 50, 915–927.

Pizzarello, S., Cooper, G.W., Flynn, G.J., 2006. The nature and distribution of the organic material in carbonaceous chondrites and interplanetary dust particles. Meteorites and the Early Solar System II, 625–651.

Poulet, F., Bibring, J.-P., Mustard, J.F., Gendrin, A., Mangold, N., Langevin, Y., Arvidson, R.E., Gondet, B., Gomez, C., 2005. Phyllosilicates on Mars and implications for early martian climate. Nature 438, 623–627.

Quinn, R., Zent, A.P., McKay, C.P., 2006. The photochemical stability of carbonates on Mars. Astrobiology 6, 581–591.

Squyres, S.W., Arvidson, R.E., Bell, J.F., Brückner, J., Cabrol, N.A., Calvin, W., Carr, M.H., Christensen, P.R., Clark, B.C., Crumpler, L., et al., 2004. The opportunity Rover's Athena science investigation at Meridiani Planum, Mars. Science 306, 1698–1703.

Stalport, F., Coll, P., Cabane, M., Person, A., González, R.N., Raulin, F., Vaulay, M.J., Ausset, P., McKay, C.P., Szopa, C., et al., 2005. Search for past life on Mars: physical and chemical characterization of minerals of biotic and abiotic origin: part 1—Calcite. Geophysical Research Letters 32, 23205.

Stalport, F., Coll, P., Szopa, C., Cottin, H., Raulin, F., 2009. Investigating the photostability of carboxylic acids exposed to Mars surface ultraviolet radiation conditions. Astrobiology 9, 543–549.

Stalport, F., Coll, P., Szopa, C., Person, A., Navarro-González, R., Cabane, M., Ausset, P., Vaulay, M.J., 2007. Search for past life on Mars: physical and chemical characterization of minerals of biotic and abiotic origin: 2. Aragonite. Geophysical Research Letters 34, 24102.

Stalport, F., Coll, P., Szopa, C., Raulin, F., 2008. Search for organic molecules at the Mars surface: the "martian organic material irradiation and evolution" (MOMIE) project. Advances in Space Research 42, 2014–2018.

Stalport, F., Guan, Y.Y., Coll, P., Szopa, C., Macari, F., Raulin, F., Chaput, D., Cottin, H., 2010) "UV-olution, a photochemistry experiment in low earth orbit": investigation of the photostability of carboxylic acids exposed to Mars surface UV radiation conditions. Astrobiology.

Thuillier, G., Floyd, L., Woods, T.N., Cebula, R., Hilsenrath, E., Hersé, M., Labs, D., 2004. Solar irradiance reference spectra for two solar active levels. Advances in Space Research 34, 256–261.

Treiman, A.H., 2008. Ancient groundwater flow in the Valles Marineris on Mars inferred from fault trace ridges. Nature Geoscience 1, 181–183.

Weiner, S., Dove, P.M., 2003. An overview of biomineralization processes and the problem of the vital effect. Reviews in Mineralogy & Geochemistry 54, 1–29.

Wu, C., 2007. Secrets of the martian soil. Nature 448, 742.