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Shielding biomolecules from effects of radiation by Mars analogue minerals and soils

G. Ertem[1], M. C. Ertem[2], C. P. McKay[3] and R. M. Hazen[4]

[1]*Department of Atmospheric and Oceanic Science, University of Maryland, College Park, MD 20742, USA e-mail: gertem@umd.edu*
[2]*Maryland Advanced Development Laboratory, University Research Foundation, Greenbelt, MD 20770, USA*
[3]*Space Science Division, NASA Ames Research Center, Moffett Field, CA 94035, USA*
[4]*Geophysical Laboratory, Carnegie Institution for Science, Washington, DC 20015, USA*

Abstract: Organic compounds have been delivered over time to Mars via meteorites, comets and interplanetary dust particles. The fate of organic material on the surface of Mars must be affected by the Martian environment, in particular by ultraviolet (UV) and other ionizing radiation. Penetration depth of UV radiation into soils is in the sub-millimetre to millimetre range and depends on the properties of the soil. The aim of this research is to study the possible protective role of Martian analogue minerals and soils for survivability of biomolecules against UV radiation and to compare their decomposition rates within a 1 mm-thick portion of the surface. Results demonstrated that minerals offer significant protection to biomolecules purine, pyrimidine and uracil against UV photolysis. In the absence of these minerals, organic compounds are completely degraded when subjected directly to UV photolysis equivalent to only 5 Martian day's exposure. However, similar UV exposure of organics dried from solution onto powdered calcium carbonate (calcite; $CaCO_3$), calcium sulphate (anhydrite; $CaSO_4$), clay-bearing Atacama dessert soil and 7 Å clay mineral kaolinite [$Al_2Si_2O_5(OH)_4$] results in only 1–2% loss of organics. Mixtures of purine and uracil with calcium carbonate exposed to gamma radiation of 3 Gy (3 Gray), which corresponds to approximately 15 000 days on Mars, results in up to 10% loss of organics. By contrast, these organic compounds completely decomposed upon mixing with iron oxide (Fe_2O_3) before UV irradiation. As the search for extinct or extant life on Mars has been identified as a goal of top priority in NASA's Mars Exploration Program and continues with several missions planned to the red planet by both NASA and the European Space Agency (ESA) in the next few decades, our findings may play a useful role in identifying optimal target sites on the Martian surface for future missions.

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Introduction

The accumulation and preservation of organic molecules at or near planetary surfaces is an essential step in life's origins. Organic species accumulate by a combination of exogenous and endogenous processes (Chyba & Sagan 1992; Hazen 2005; and references therein; Love & Brownlee 1993). At the same time, organic molecules may decompose through a variety of chemical and physical processes, including thermal degradation, mineral-mediated oxidation and photolysis (Bada *et al.* 1995; Bada & Lazcano 2002; Ten Kate *et al.* 2005; Marshall-Bowman *et al.* 2010; Kim *et al.* 2013). As models of Martian meteoritic influx have suggested, considerable amounts of carbonaceous meteoritic materials should be present in the Martian regolith (Flynn & McKay 1990; Bland & Smith 2000). Calculations by Kanavarioti & Mancinelli (1990) based on the stability of amino acids revealed that remnants of these compounds, if they existed on Mars 3.5 billion years ago, might have been preserved buried beneath the surface-oxidizing layer. Therefore, assessing the stability of organic species in near-surface environments is one key to evaluating plausible scenarios for the origins of life.

The low level of organics on Mars has been puzzling because organic matter should be delivered continuously to the Martian surface, as it is to the Earth, from space via meteorites (Cronin & Chang 1993; Sephton *et al.* 2002; Pizzarello *et al.* 2006), comets (Llorca 2005) and interplanetary dust particles (Schramm *et al.* 1989; Flynn 1996). However, exposure to ionizing radiation by charged, energetic particles arriving at the surface through the thin Martian atmosphere suggests that the fate of these organic molecules at or near the Martian surface must be very different than those on the Earth (e.g. ten Kate *et al.* 2005).

Accordingly, we are investigating the possible protective role of Martian analogue powdered minerals and soils for the survivability of biomolecules. Here, we report on the protective roles of Martian analogue minerals and soils against effects of ultraviolet (UV) and gamma radiation for purine, pyrimidine and uracil. Since RNA and DNA can be considered as

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derivatives of purine, pyrimidine, and uracil, these bases are crucial biomolecules in scenarios of prebiotic molecular organization, as well as in extant living systems.

The detection of organics on Mars by SAM at Gale Crater has been hampered by the contamination of the instrument by the derivatization reagents *N*-tert-butyldimethylsilyl-*N*-methyltrifluoroacetamide (MTBSTFA) and dimethylformamide and by the presence of perchlorate (ClO_4^-) in the soil and sediments (Glavin *et al.* 2013; Leshin *et al.* 2013). The SAM results are consistent with the discovery by the *Phoenix* Wet Chemistry Laboratory of 0.6 wt.% ClO_4^- in the soil (Hecht *et al.* 2009; Kounaves *et al.* 2009). These discoveries suggest that ClO_4^- is global in extent and that ClO_4^- or intermediary oxychlorines such as ClO_2^- or ClO^- may be participants in the destructive oxidation of organics and/or their lack of detection by *Viking* and the Mars Science Laboratory (Navarro-González *et al.* 2010) and the reactivity detected by the *Viking* Biology Experiments (Quinn *et al.* 2013). A single organic, chlorobenzene, detected by SAM in a sample from the mudstone deposits at Yellowknife Bay in Gale Crater has been determined to derive from Martian organics (Freissinet *et al.* 2015). The chlorobenzene detected is a reaction product of some unknown Martian organic species and, fortuitously, chlorobenzene does not appear as a strong reaction product of the MTBSTFA contaminant with perchlorate.

Methods

Materials

Calcium carbonate (calcite; $CaCO_3$), calcium sulphate (anhydrite; $CaSO_4$), ferric oxide (Fe_2O_3), purine, pyrimidine, uracil and high-performance liquid chromatography (HPLC) grade acetonitrile were purchased from Sigma-Aldrich, St. Louis, MO. Atacama Desert soil was provided from Dr. Chris McKay's collection: ATC 01-6. It contains phyllosilicates, kaolinite and salts (Sutter *et al.* 2006). The 7 Å clay mineral kaolinite [$Al_2Si_2O_5(OH)_4$, reference sample KGa-1b, 1127] was purchased from Source Clays Repository – The Clay Minerals Society. All of these minerals have been identified in Martian surface soil and are expected to have been significant mineralogical components of both Earth and Martian soils throughout most of their histories (Hazen 2005, 2013).

All glassware was wrapped in aluminium foil and heated at 500°C for 3 h before each use. Concentrations of purine, pyrimidine and uracil were measured by HPLC using an Alltech Alltima C-18 reverse phase column (Ertem *et al.* 2007).

Preparation of minerals, removal of organics from minerals and soil samples

Minerals were washed three times with water (18 MΩ, Milli-Q; 150 mL/10 g of each mineral), once with methanol, and a final wash with water. Samples were then freeze-dried at −85°C and at 20–25 mbar for 24 h to remove water, where water and methanol, if any remained, undergo sublimation, to produce a fine powder. Further removal of organics from kaolinite and Atacama soil was carried out according to the procedure described in Wattel-Koekkoek *et al.* (2001): Following the water–methanol–water washings, minerals were shaken in aqueous 0.1 M $Na_4P_2O_7$ solution, dialysed and freeze-dried. Organic-free minerals were passed through an 80 mesh sieve, which corresponds to a maximum particle size diameter of 177 μm, to obtain a product with uniform particle size distribution.

Preparation of organic compound – mineral mixtures for UV irradiation

The extent of binding of organic compounds to varied minerals varies with the structure of the organic molecules and the nature of the mineral (e.g. Ferris *et al.* 1989; Hazen 2006). In order to have comparable quantities of each organic compound in each soil–organic mixture, physical mixtures of minerals with organic compounds were prepared and used throughout this research. We used 400 mg of mineral/soil powder for each experiment. We also established the volume of the organic compound solution required to completely wet the mineral without leaving excess solution above the surface of the powdered minerals. We then added the aqueous solutions prepared to contain 25 ppm of organic compound and 0.6% sodium perchlorate per 400 mg of each mineral.

Mineral–organic mixtures prepared for UV irradiation as described above were freeze-dried and placed onto aluminium plates with 3.0 cm diameter and 1.0 mm height, making sure that the surface of the organic compound–mineral mixture was optically flat and with a thickness of 1 mm. This experimental step is the most time-consuming and crucial, especially with hygroscopic minerals. Note that the penetration depth of UV light into soil, which depends on the wavelength and particle size, is about 1 mm or less (Sagan & Pollack 1974; Keppler *et al.* 2012).

Controls

(a) *Non-irradiated samples*: Three sets of each organic compound (purine, pyrimidine or uracil)–mineral mixture were prepared as described above. For each organic compound–mineral pair, one set was kept as control (i.e. was not irradiated), while two sets were UV-irradiated. Organic compounds were extracted from the mixtures of organics with calcium carbonate and calcium sulphate (both the controls and UV-irradiated samples) by shaking them with water and removing the extracts after centrifugation at 4000–6000 rpm for 30 min. This procedure was repeated three times. Three extracts were combined for each sample and solutions containing the organic compounds were freeze-dried. Freeze-dried samples were dissolved in 1.0 mL of water for HPLC analysis. Extraction of organics from Atacama soil– and kaolinite–organic mixtures was accomplished by two water extractions followed by one 0.1 M aqueous sodium pyrophospahate, $Na_4P_2O_7$, extraction. Combined extracts were freeze-dried, dissolved in 1.0 mL of water, dialysed and analysed by HPLC (see Table 2).

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Table 1. *Parameters used in the simulation chamber and nominally present on Mars*

		Simulated conditions in MSC: UV source: Oriel 6258	
	Martian condition[a]	Lamp irradiance: W m^{-2} nm^{-1} at 0.50 m	Actinometer reading: W m^{-2} nm^{-1} at 0.16 m
UV radiation (nm)	>200	>200	
UV intensity in W m^{-2} nm^{-1}	At 239 nm 0.006[b]		
At 254 nm: UV intensity (m^{-2} nm^{-1})		0.010	0.028
At 302 nm: UV intensity (m^{-2} nm^{-1})		0.012	0.029
At 365 nm: UV intensity (m^{-2} nm $^{-1}$)		0.013	0.030
Temperature (°C)	−123 to +25	−196 to +25	
Gas composition (%)	CO_2: 95.3; N_2: 2.7; O_2: 0.13	CO_2: 95.3; N_2: 2.7; O_2: 0.13[c]	

[a]From Horneck *et al.* (2000).
[b]Annual average intensity at 11.6°N (personal communication between Horneck & Patel).
[c]Custom prepared by Roberts Oxygen Company.

(b) *UV irradiation of organic compounds in the absence of minerals*: The same volume of organic compound solution added to the minerals was placed onto aluminium plates, freeze-dried and UV irradiated in the absence of minerals under the same conditions employed for organic compound–mineral mixtures. After irradiation, aluminium plates were washed off with 1.0 mL of water three times. Combined extracts were freeze-dried, dissolved in 1.0 mL of water and analysed by HPLC.

UV irradiation experiments

UV irradiation of the organics in the absence of minerals and of mineral–organic compound mixtures were performed in a Martian Simulation Chamber at the University of Maryland under conditions mimicking the Martian surface, as listed in Hansen *et al.* (2005) (Table 1). This chamber [Fig. 1(a) and (b)] consists of a stainless steel cylindrical assembly with an internal diameter of 25 cm and depth of 45 cm. The spectral irradiance of the 300 W ozone-free 6258 xenon-arc lamp, which provides collimated UV light, was measured using an actinometer at three wavelengths (Table 1).

The UV light was directed through a quartz window to mineral–organic mixtures containing 0.6% sodium perchlorate – a concentration similar to that found on Mars by *Phoenix* (Hecht *et al.* 2009; Kounaves *et al.* 2009).

One set of duplicate mineral–organic compound samples was irradiated at 15–25 millibar, while the second set was irradiated at ambient pressure.

The dose of UV radiation received by the samples during 30 h was equivalent to 5 Martian Sol (Sol: Martian day = 24 h 37 min): 0.028 W m^{-2} nm^{-1}.

Gamma irradiation experiments

For comparison, we also studied the effects of gamma radiation on mineral–biomolecule mixtures. Gamma rays have considerably higher energy [$>2 \times 10^{-14}$ J (Joule)], compared with UV radiation (5×10^{-19}–2×10^{-17} J). Samples were prepared as described for UV irradiation experiments: organic–mineral mixtures were placed in 2 ml polyethylene tubes.

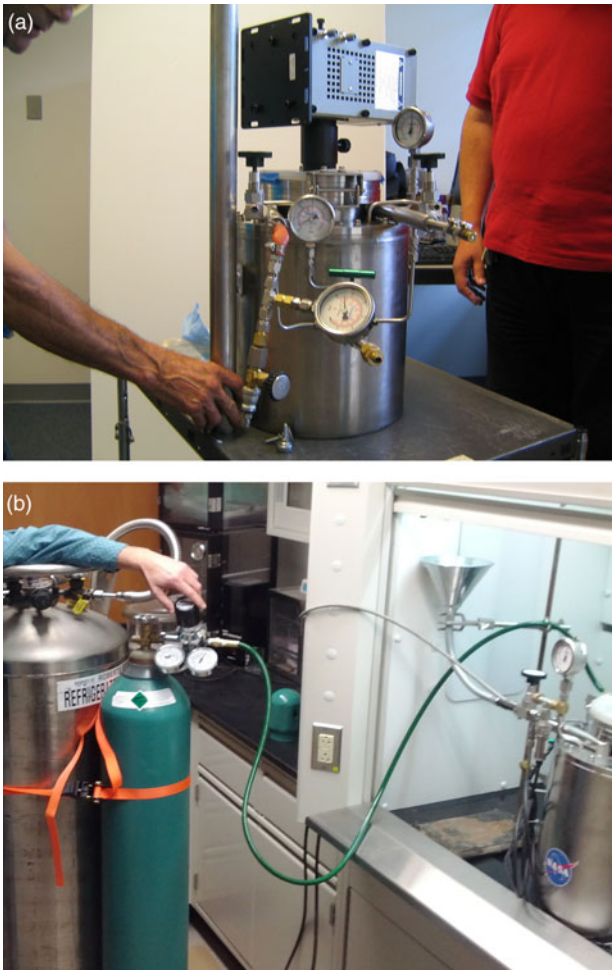

Fig. 1. (a) Mars Simulation Chamber. (b) Mars Simulation Chamber-Gas tanks containing liquid nitrogen and Martian atmosphere gas mixture (gas mixture was custom prepared by Robert Oxygen Company, Rockville, Maryland).

Irradiation was performed at the Uniformed Services University, Bethesda, MD using Gamma Cell 40 from a ^{137}Cs source at 25°C. Although Cs-137 itself is a beta emitter with a half-life of 30.1 years, its decay product metastable Ba-137 further decays by gamma emission to the stable

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Table 2. *Results showing the percentages of organic destroyed after 30 h of UV irradiation under conditions listed in Table 1. As explained in the text, experiments were run in duplicates*

	$CaCO_3$–organic solution + UV	$CaSO_4$–organic solution + UV	Atacama–organic solution + UV	Kaolinite–organic solution + UV	Organic solution, NO mineral + UV
Purine	2.1–2.3	1.3–1.9	2.1–2.3	1.3–1.5	100
Pyrimidine	1.8–2.0	1.8–1.9	1.0–1.4	1.0–1.2	100
Uracil	2.0–2.1	1.8–1.8	n. d.	0.19–0.20	100

Predetermined volumes of solutions to wet each mineral–organic mixture containing 25 ppm organic compound and 0.6% $NaClO_4$ were added to each 400 mg of mineral. The mixtures were freeze-dried and irradiated in the Martian simulation chamber. One set of samples was irradiated at ambient pressure, while the second set was irradiated at 15–25 millibar. As controls, the same amounts of organic compounds added to the minerals were irradiated under the same conditions but in the absence of minerals. Organics were extracted from the minerals and analysed by HPLC along with the organics irradiated in the absence of minerals.

Organic compounds were completely decomposed by oxidation when they were mixed with Fe_2O_3 before being subjected to UV light. These results are not included in Table 2.

Table 3. *Percentages of organic lost after 13 Gray gamma irradiation*

HPLC analysis of purine and uracil extracted from mineral–organic mixtures before and after gamma irradiation

Mineral–organic	Samples gamma irradiated in wet state (mAU)	Samples gamma irradiated in wet state (mAU)	Control samples received no gamma radiation	% Lost in wet state	% Lost in dry state
$CaCO_3$–Purine	86	85	98	12	13
$CaCO_3$–Uracil	268	268	297	10	10

Biomolecule–mineral mixtures were irradiated with gamma radiation from a ^{137}Cs source, extracted and organics were analysed by HPLC. Numbers indicate in mAU (milli Absorption Units) obtained by HPLC.

Ba-137 with a half-life of only 2.6 min. In the Gamma Cell 40, electrons are trapped before reaching the target sample. In these experiments, samples received a total dose of 3 Gy (3 Gray) corresponding to approximately 15 000 days dosage on the Martian surface (Hassler *et al.* 2014).

Results

Results of UV irradiation for 30 h (equivalent to 5 Martian Sol irradiation) shown in Table 2 indicate only a minor loss of organic compounds (<2%) when they are mixed with Mars analogue minerals/soils. Furthermore, the extent of loss does not vary with pressure in the chamber during irradiation. UV-irradiated purine, pyrimidine and uracil in the absence of minerals completely decompose to compounds without any chromophore group(s) in their structure.

Irradiation performed in the absence of perchlorate ions, where chlorine is at its highest oxidation state of 7+, produced comparable results (i.e. 1–2% loss of organics). In comparison, gamma irradiation of mineral–organic mixtures with a dose of 3 Gray corresponding to ∼15 000 days on the Martian surface (Hassler *et al.* 2014) results in about 10% loss, as shown in Table 3.

Discussion

These results are in sharp contrast to the behaviour of mixtures of purine, pyrimidine and uracil with Fe_2O_3, which decomposes these compounds in ambient light upon mixing, before UV irradiation. Similarly, rapid photo-oxidation has been observed for other transition metal oxides, for example in the rapid decomposition of the pentose sugars arabinose, lyxose, ribose and xylose in the presence of rutile (TiO_2) under ambient light conditions, but not in darkness (Klochko *et al.* 2012).

These results do not necessarily distinguish whether the loss of organics occurred only at the very outer surface of mineral–organic mixtures or throughout the whole mixture. It is conceivable, for example, that some of the 1–2% loss of organics during irradiation of samples was due to the location of organics; that is, it is possible that organic species situated on the exposed outer surface of mineral–organic mixtures, namely above the penetration depth of UV radiation, were not protected by the minerals/soils.

Kaolinite, which has a layer structure made up of one tetrahedral sheet and one octahedral sheet, does not strongly bind biomolecules studied here. We are currently investigating the protective role of clay minerals composed of three-sheet layers with varying charge densities, namely phyllosilicates (charge density arises from the isomorphic substitution of Al^{3+} ions in the octahedral sheet by Mg^{2+} ions and Si^{4+} ions in the tetrahedral sheets by Al^{3+} ions. It is counterbalanced by the equivalent number of interlayer cations, mostly Na^+ or Ca^{2+}, held in the interlayer region of the clays). Phyllosilicates, along with sulphates, have been identified on Mars in the southern hemisphere (Bibring *et al.* 2005). Since The Wet Chemistry Laboratory on the *Phoenix* Lander Mission can analyse the chemistry and mineralogy of the soil (Kounaves *et al.* 2009), the charge density of the smectites can be calculated from chemical analysis data (Köster 1977).

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The extent of smectites' ability to serve as catalyst for the formation of RNA-like oligomers widely varies with their charge density (Ertem *et al.* 2010). Our research designed to test the protective effect of smectite with varying charge densities against radiation will demonstrate the correlation, if any, between the charge density and the protective effect (that is, whether the protective effect of three-sheet smectites varies with the charge density of the mineral). These studies in turn will provide useful information to find the best target sites to look for organics on the Martian surface. Although the presence of perchlorate ions in Martian soil has been established by several groups, we did run a set of experiments in the absence of perchlorate ions and obtained comparable results.

Results of the UV irradiation carried out at 15–25 millibar and at ambient pressure were comparable and demonstrated that pressure has no significant effect on the irradiation products, as was also shown by previous research (Horneck *et al.* 2000; Schuerger *et al.* 2003, 2006).

Conclusions

We have chosen to study the survivability of purine, pyrimidine and uracil against the effects of UV and gamma radiation because RNA and DNA are derivatives of these biomolecules. Our results demonstrate that in the absence of minerals, or in the presence of ferric oxide, purine, pyrimidine and uracil decomposed into products without any chromophore group. If they turned into gaseous products upon being exposed to UV irradiation, it would have been very difficult to determine their identity under the 98% CO_2 atmospheric conditions of the experiments.

In the presence of powdered minerals and soil analogues, by contrast, these organic species are largely preserved in surface layers only about 1 mm thick, and the extent of preservation does not vary with the nature of the mineral/soil.

A number of missions to Mars and other planets are being planned to search for organic molecules and possible biosignatures. Therefore, it is of the utmost importance to investigate the survivability of organics under plausible surface conditions on the surface of each planet. Our results demonstrated that 25 ppm (which corresponds to 25 mg of organics per kilogram of soil) of purine, pyrimidine, and uracil mixed with soils present on the Martian surface would enjoy the possible protective effect of minerals, as was first proposed by Bernal (1949) as early as in 1947 (published in 1949).

These experiments also point to the need for additional research. For example, studies in preparation of organic survivability in layers both significantly thinner and thicker than 1 mm with a wider range of minerals and soils may reveal the extent to which mineral–molecule interactions, potentially independent of UV or visible light flux, lead to organic survival or degradation.

Currently, we are investigating the effects of gamma radiation, asteroid impacts and cosmic radiation and particles on the survivability of a suite of biomolecules and alkyl derivatives of sulfonic acid and phosphonic acids in the presence and absence of Martian analogue minerals. Results of gamma irradiation indicated that purine and uracil undergo a 10–13% lost upon irradiating the $CaCO_3$–purine and $CaCO_3$–uracil mixtures with gamma rays of 3 Gray, which corresponds to a dosage equivalent to ~15 000 days on the Martian surface. Experiments designed to study the effects of gamma radiation at a dose corresponding to 500 000 years and 1 000 000 years on the Martian surface are in progress.

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