

Response of organics to simulated Martian conditions

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Background

It is believed that Mars in its ancient past had many characteristics thought to be similar to those of the early Earth. Of particular interest is the notion that liquid water has been a significant geological process in terms of landform erosion and chemical alteration, judging by relict fluvial valleys and, at a smaller scale, concretions seen on the present day martian landscape. However, whatever similarities Mars might have had with the Earth are now greatly diminished. The martian atmosphere is presently almost totally devoid of water, and in its liquid form water cannot persist at the surface. Furthermore, unlike the Earth and its widespread chemical indications of microbial life, no evidence for the presence of native organic matter has been found. Indeed, the loss of liquid water from Mars' surface and the removal of protective atmospheric components suggest that if life of some type did arise on Mars then the present surface may not be a part of that biosphere, if terrestrial biology is taken as a guide. However, if there has *never* been an active ecosystem on Mars, then the surface should not be totally devoid of organic carbon; meteoritic infall ought to result in measurable levels of carbon-bearing compounds in the surface regolith. The seeming lack of detectable organic compounds on Mars is a mystery and one which has important implications for the viability of Mars as a host for life, for the ongoing challenges of planetary protection, and eventually, the day-to-day problems of environmental material compatibility.

This chapter summarizes present research on how aspects of the martian environment alter the stability of organic compounds, with emphasis on chemical species of relevance to microbial processes and the question of the origin of life.

1. The problem: absence of evidence, or simply absence?

Despite the recent data gained from rovers and orbital spacecraft, our knowledge of Mars' surface chemical make-up is scant. Only sites within two regions¹ have been examined with an equipment suite suited to organic chemistries, and employing a Gas Chromatograph-Mass Spectrometer (GCMS). These physically sparse data sets suggest that there are a number of candidate processes at work on the surface of Mars which degrade carbon-based compounds and the planetary community has sought to identify and characterize these reactions. The rationale for such studies has support from several diverse fields; from the purely practical viewpoint of selecting appropriate materials for spacecraft components, to the deeper question of whether Mars may have been an abode for life in some form in its past. It should be noted that

¹ Chryse Planitia and Utopia Planitia, landing sites of the Viking 1 and 2 spacecraft respectively.

the absence of evidence for organic matter at the sampling sites of the Viking landers is also a function of the detection limits of the analytical payloads of those spacecraft. Klein (1978) pointed out that tenuous microbial communities with numbers $< 10^6$ cells would have been invisible to the experiments performed by the landers. Thus the Viking data do not rule out the presence of native organic matter. Indeed the low limit to detection of ~ 80 ppb when averaged over all species sought for, (Biemann et al., 1977), combined with the difficult-to-interpret results of the Viking labelled-release experiment suggest that organic matter in the martian surface, if present, is exposed to an unusual chemical environment.

Organic compounds formed during an early active pre-biosphere or even the decay products of now-extinct organisms, are not the only material that might be sought on Mars. If, as is possible, there has never been an active ecosystem on Mars, any organic matter found on that world would have to have been produced by abiotic means and the meteoritic delivery of organic compounds is a prime example of such a process. Mars, like all bodies in the Solar System, experiences meteoritic bombardment. With a mass one-tenth that of the Earth, Mars should experience a lower overall flux of meteorites than the Earth, but its close proximity to the asteroid belt instead is predicted to lead to an areal flux that is greater than the terrestrial infall rate (Shoemaker, 1977). Of the terrestrial meteorites which have been found and studied, around one in five carries a high amount ($\sim 3\%$ by weight) of carbon in the form of organic molecules – and these are identified by the term carbonaceous chondrite. Much of this carbon is locked up in an insoluble macromolecular form (Hayes, 1967) that resists acid solvation. The remaining soluble compounds are notably diverse in type², ranging from the simplest amino acid (glycine) to fullerenes such as the eponymous C_{60} , with the abundance of a given molecule generally falling with increasing carbon number (Cronin and Chang, 1993).

There are no reasons to suspect that the types of objects striking Mars differ substantially from those found on the Earth. Thus, along with meteorites, Mars ought to have experienced cometary impacts, although the rarity of this process and the poorly understood nature of the impactor makes the total carbon mass-flux difficult to estimate. Macroscopic impactors such as meteorites or comets are not expected to provide the sole input of organic matter to Mars. Interplanetary dust particles (IDPs) are micron-size porous aggregates of silicates, some of which appear to be associated with volatile-rich objects such as long and short-period comets. The ubiquity and population size of IDPs in the Solar System allows tighter estimates of their impact rates to be made and it has been estimated that IDPs may be responsible for showering the surface of Mars with over twenty tonnes of carbon per year (Flynn, 1996), leading to an areal mass flux of a little under $2 \mu\text{g m}^2 \text{yr}^{-1}$. If both meteorites and IDPs are considered, then Mars ought to have a surface organic component in the order of kilogrammes per m^2 . Clearly, this is not the case as Mars cannot be treated as a static planet. In reality several competing dynamic equilibria are likely to be at work, governing the rate of infall and those processes that destroy and garden the meteoritic debris deeper into the regolith. In figure 1 some of the competing processes are illustrated which either deliver or potentially destroy material in the

² Typical concentrations being of the order of 10^1 to 10^3 ppm, depending on compound and meteorite, see Botta and Bada (2002) for a review.

martian near-surface, a description which will include the lower troposphere and that fraction of the crust which experiences seasonal changes in temperature and water ice content.

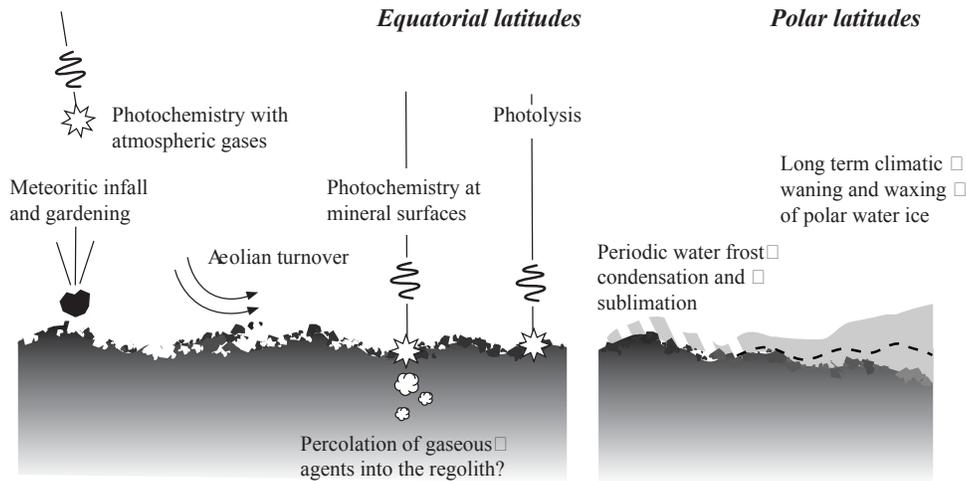


Figure 1 – Some of the processes at work in near-surface environments of Mars at low and high latitudes.

With these processes in mind, the insolation experienced at Mars, and the chemical implications of its atmosphere will be discussed.

2 The martian environment - lighting

The intensity of light arriving from the Sun at Mars' is around 600 Wm^{-2} , less than half that experienced at Earth's orbit. However, the absence of a substantial ozone layer in Mars' atmosphere and a similarly low level of water vapour make the lighting spectrum experienced at the surface very different from that found on Earth. The insolation spectra at the noon-time equators of Mars and Earth are shown in figure 2 for clear-sky conditions, adapted from Mecherikunnel et al. (1983) and Córdoba-Jabonero et al. (2003).

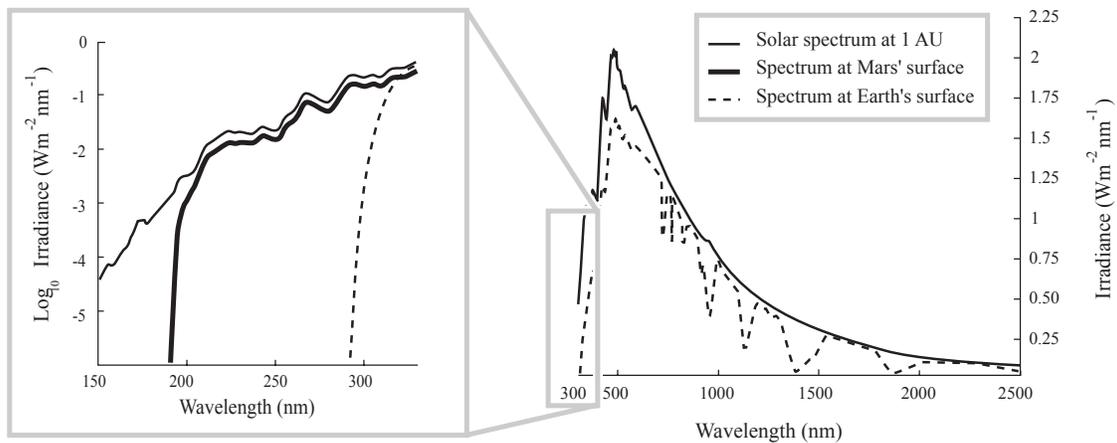


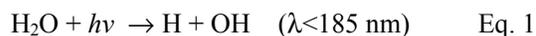
Figure 2 – Comparative spectra of noontime lighting at the equators of Mars and Earth. Note the use of a logarithmic scale in the left-most chart.

From a photochemical point of view, the most significant difference between martian and terrestrial lighting spectra is the presence of ultraviolet light with wavelengths shorter than 500 nm, as shown in the left-most chart of figure 2. The lighting experienced at Mars is essentially solar, although shortward of 200 nm the carbon dioxide in the atmosphere is an effective filter as CO₂ is readily dissociated by light with a wavelength shorter than 2275 Å. Thus, the atmosphere becomes increasingly opaque to light below this value, as is shown in the rapid turn-down in the surface irradiance in the left-most chart of figure 2. At a wavelength of 200 nm the average photon has an energy of 6 eV, comparable to the binding energy of a C=C bond and almost twice the C-O bond energy. Such energetic quanta cause photolytic reactions in both solid and gaseous species and some of these reactions have a biological importance either via the direct photolysis of compounds, or through the generation of reactive species.

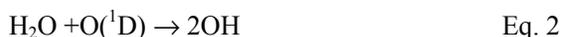
3 The martian environment - atmosphere

Early telescopic observations of Mars revealed a tenuous atmosphere (Kuiper, 1955) and indications of seasonal polar changes. Reportedly observed first by Huygens and Cassini in 1666 and 1672 respectively (Slipher, 1962), the bright material at the poles of Mars was tacitly assumed to be mostly water ice. Although the condensation and sublimation of carbon dioxide is responsible for the seasonal polar change, there is indeed a water ‘cycle’ on Mars, albeit much weaker than that on Earth. At present, the low surface pressure of Mars’ atmosphere prevents liquid water from being a stable feature of the landscape, although regions of the surface do become significantly warmer than the triple point of water. The small amount of water vapour in the atmosphere therefore takes part in a cycle of sublimation and condensation, with seasonal micron-thick frosts of water ice appearing in near-polar regions.

The low level of water in Mars’ thin atmosphere leads to a near-solar spectrum above 200 nm, and also enables a complex cycle of photochemical reactions despite being present at low concentrations, with a global average surface partial pressure of ~0.13 Pa (~10⁻³ mbar) as modeled by Schorghofer and Aharonson (2004). Water vapour in can generate the aggressive hydroxyl (OH) radical by simple photolysis as shown in equation 1, although the optical filtering imposed by CO₂ at ~ 200nm greatly restricts this reaction at the surface.



The hydroxyl radical can also be generated by excited oxygen, which in turn can be produced from the dissociation of ozone, as,



These are by no means the only pathways to radical formation, and Nair et al. (1994) provide a comprehensive review. One effect of the OH and H radical production is that they mediate the recombination of O₂ and CO (formed from CO₂ photolysis) and in doing so prevent the CO₂ atmosphere from being converted into CO and O₂.

Other reactions of a biochemically important nature are expected from the atmosphere of Mars, and the formation of hydrogen peroxide is notable as this oxidant is a solid at martian temperatures. Once formed, OH radicals can dimerize to hydrogen peroxide (H₂O₂) although other formation paths are possible and the formation rate of H₂O₂ may be enhanced through phenomena such as electrical discharges (Farrell et al., 2005) caused by tribological grain charging. The formation of H₂O₂ is ultimately dependent on the concentration of water vapor in the atmosphere and in particular its near-surface partial pressure.

With the potential for radicals and solid-phase oxidizing agents to form, a number of pathways for the degradation of organic molecules become available. The following table is adapted from Benner et al. (2000) and is not meant as an exhaustive reference. For some of the compounds present in the Murchison carbonaceous chondrite, the chemical products resulting from OH radical destruction are listed.

Table 1 Expected metastable products from radical-mediated oxidation of organic compounds of the Murchison meteorite.

| Compound family | Conc. in Murchison (ppm) | Product | Martian conditions |
|------------------------|--------------------------|-------------------------|--|
| Acid insoluble kerogen | ~14500 | Benzenecarboxylic acids | Solid at martian surface |
| Aromatic hydrocarbons | 15-28 | Benzenecarboxylic acids | .. |
| Aliphatic hydrocarbons | 12-35 | Acetate | Can be present as solid or gas (condenses at 190K) |
| Alcohols | 11 | Acetate | .. |

4 Mars in the laboratory; simulation

A necessity of planetary spacecraft engineering is the construction of a suitable facility for testing the response of payload sensors. For Mars, the gross physical properties of the environment at its surface are relatively easily recreated in terms of the temperature and pressure. Problems in the choice and design of an experimental chamber begin with the type of chemical research that is frequently pursued by such Mars ‘simulators’; namely, attempting to determine how organic matter might be destroyed in the near-martian surface environment. By their nature, a simulation chamber has to be occasionally opened up to ambient laboratory conditions and this necessity brings with it problems of contamination control, which are usually solved via appropriate pumps, filters, and handling protocols. For chemically sensitive work, an extra difficulty presented by the martian surface is its highly desiccated state. Stainless steel is a common construction material for simulation vessels and because water is readily adsorbed by this alloy, achieving low levels of humidity leads to prolonged pump-down times or careful chamber design to permit baking procedures; examples of outgassing rates are readily found in the aerospace literature (Chun et al., 1996).

Providing an accurate match to the insolation at the martian surface is more challenging; broad spectral matches can be obtained with appropriately filtered xenon discharge lamps and the UV component of the martian lighting spectrum can be generated partially with deuterium discharge lamps. In attempting to

study phenomena that take place under continuum lighting it is important to distinguish between the effects caused by different parts of the lighting spectrum. Thus, near-monochromatic sources such as mercury discharge lamps, do have a place in photochemical research, but only if comparative experiments are performed that use other lighting sources so that the action spectra can be established.

Groups studying processes that are thought to be associated with the martian surface have employed a wide variety of equipment types both for simulation vessels and analytical devices. When seeking a means of exposing material to low pressures under non-terrestrial lighting, a traditional approach is to co-opt an existing vacuum system used for space simulation. Such equipment tends to be equipped with high-capacity pumping systems and is often scaled for easy manipulation of spacecraft components. This type of arrangement is exemplified by the Mars chamber operated within the European Space Agency's ESTEC division, and shown in figure 3.

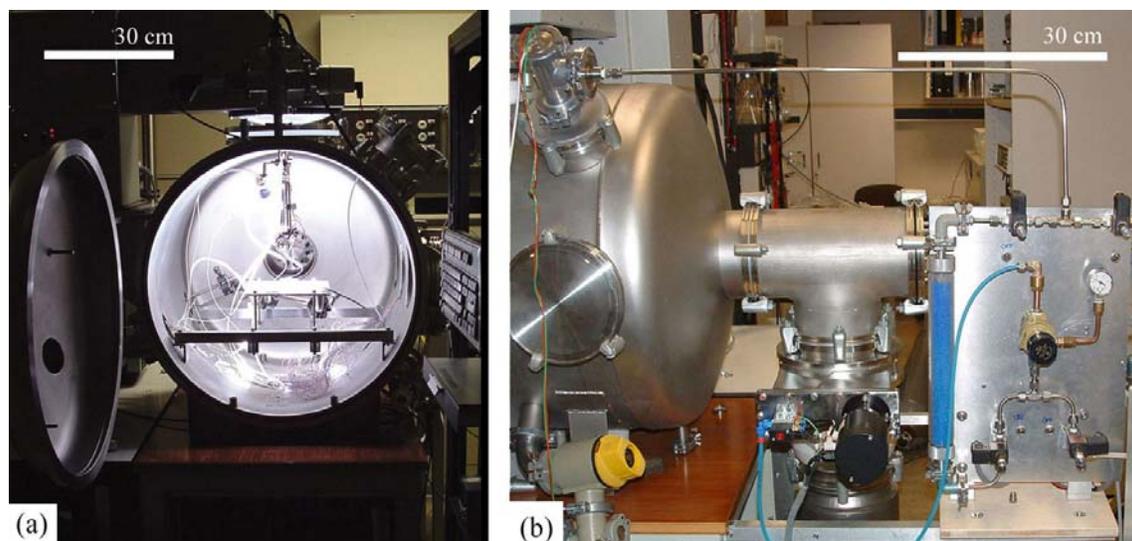


Figure 3 – A ‘traditional’ Mars simulation vessel complete with solar simulator. Note the dimensions and the use of a desiccation column for purge-air (blue vertical tube) in the right-hand image.

Such large facilities are well-suited to the study of macroscopic features of planetary environments, and are an important step to the testing of flight-versions of spacecraft payloads. Smaller chambers also have their uses in that they are inherently easier to keep clean and can even be accommodated *within* existing analytical equipment. An example of such a system is shown in figure 4. Here, a chamber with a volume of around 0.5 l is held within the optical path of an infra-red (IR) spectrometer. Through the use of a cryogenically cooled turntable, samples can be held at martian surface temperatures in the presence of a broadband UV light source in an ambient low pressure gas. Note, both of the illustrated chambers are single-wall construction and so do not provide a correct radiative or gas temperature environment for Mars. However, experiments *in vacuo* allow gas-phase processes to be distinguished from purely photolytic reactions, allowing the different niches offered by Mars' environment (shaded, buried etc.) to be modeled.

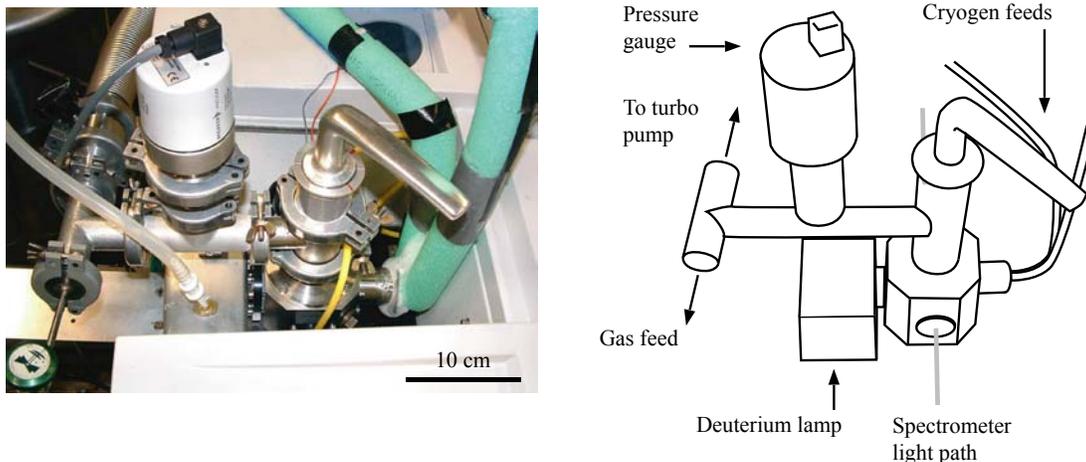


Figure 4 – A photograph and diagram of a miniature Mars chamber used for spectroscopic studies. Windows of UV-grade quartz and KBr are used for the lamp and IR light-paths respectively.

The use of non-invasive techniques such as spectroscopy has several advantages. Rather than inferring the degradation of a material through the formation and detection of a compound, IR spectroscopy directly measures the presence or absence of the material being exposed in a quantitative manner. No handling of the sample is needed for the analysis and the sample is hermetically sealed from the laboratory environment. For IR spectroscopy to work, the samples must be sufficiently thin for most of the probing IR light to pass through the material, and for amino acids this necessitates using films less than 1 micron thick applied to substrates which are IR transparent, such as silicon. A novel technique for preparing such materials is described in ten Kate et al. (2005), and the process has been used to make micron-thick layers of substances with molecules as large as C60.

With such equipment the response of simple amino acids (glycine, and D-alanine) to Mars-like conditions has been directly observed at both room temperature and also at temperatures (210K) comparable to the average equatorial surface of Mars. Photolytic degradation is measured to have a half-life of around 250 hours for glycine at martian temperatures and lighting conditions. Raised temperatures (300K), similar to the peak possible equatorial temperature on Mars, lead to a ten-fold reduction in the half-life and the degradation rate and its temperature dependence do not appear to be modified by the presence of additional carbon dioxide (ten Kate et al., *submitted*). Thus, a geographic distribution of photolytic stability could be estimated for compounds studied in this way, on the basis of annual temperature and insolation levels combined with half-life data for the material.

5 Surface chemistry

Many of the studies performed since the days of the Viking mission have examined the effect of mineral surfaces on the degradation processes associated with organic matter exposed at the surface of Mars (Oró and Holzer (1979), Huguenin R.L. et al. (1979), Stoker and Bullock (1997), Yen et al. (2000), etc.). The introduction of any mineral component raises the complexity of an experiment dramatically when

compared to simple irradiation studies of a single compound. In coming from an outdoor environment, mineral surfaces are host to chemisorbed and adsorbed volatiles such as water and the removal, or at the very least, the characterization of adsorbed water and other contaminants is difficult if the material is not to be altered; crystallographic changes can arise from heating to as little as 400K (Neal, 2000). Identification of the significant organic contaminant make-up of existing regolith standards, such as Mars-1 (Allen et al., 1998) from the Johnson Space Center, is a necessary step when such materials are used as analogues for martian surfaces. Indeed, with no prior cleaning, two commonly available regolith analogues have been shown to be ill-suited for detailed studies of the response of organic matter to the martian environment owing to the extant biological contamination present therein. Garry et al. (2005) characterized the amino acid content of simulants with high-performance liquid chromatography which showed the presence of over a dozen amino acids with average concentrations of 10ppm. Such contamination is in-line with other studies which have demonstrated the presence of bacterial spores in the Mars-1 analogue (Mendez et al., 2005), a predictable outcome for a material that was never designed to be a match for the low organic content of the martian regolith.

Experimental studies with single-component minerals have emphasized the role that adsorbed water can play, and it is possible that the presence of quasi-liquid films of water is critical to the formation of oxidizing agents. The low but non-zero humidity of the martian atmosphere implies that water will be present on surfaces in diffusive contact with that gas. If water adsorbed onto a mineral grain can leach soluble species from the rock, then the ‘photo-Fenton’ reaction (abbreviated from Walling, 1975) can occur, namely;



This process is well known on Earth (Southworth and Voelker, 2003) and has been postulated as an explanation for the rapid destruction by oxidation of organic species (Benner et al., 2000 and Möhlmann, 2004). The perhydroxyl radical formed from this reaction is more vigorous than the hydroxyl radical which is commonly used to degrade organic matter in industrial processes. Clearly, the process is limited at the surface of Mars by the availability of aqueous iron salts, and the presence of hydrogen peroxide, which can be generated separately from water vapour, as mentioned in section 3. Notably, the above reaction requires solvation of the iron species, and at first glance such a scenario is unlikely for the desiccated surface of Mars. However, quasi-liquid films of unfrozen water can persist on mineral grains cooled to temperatures comparable to those found on Mars, with the film thickness governed by the ambient humidity. The amount of water vapour needed to produce a monolayer of water at the conditions found at surface of Mars is not large; the martian surface partial water vapour pressure of around 10^{-3} mbar is used in a theoretical model presented by Möhlmann (2004) to predict an equilibrium state in which a few (~5) monolayers of water would be ubiquitous on exposed Martian surfaces. This quasi-liquid water layer would vary in thickness throughout the martian year, waxing and waning with the temperature of the local atmosphere.

Condensed water can play other roles in the formation of other aggressive chemical agents. The exposure of thin water frosts on iron-bearing minerals to UV has been shown to cause the release of oxygen upon warming (Huguenin *et al.*, 1979), arising from the formation of a condensed oxidizing agent at the mineral surface. Later experiments with feldspar by Yen *et al.* (2000) demonstrate that superoxide radicals such as O_2^- are formed through the combination of cold mineral surfaces (-30 °C), Mars-like UV lighting, free oxygen, and low concentrations of water. The quantum efficiency for this process has been estimated by Yen *et al.* (2000) as being 10^{-6} radicals photon⁻¹, a low but non-negligible rate. This destruction rate, and that associated with the interaction of oxygen and UV irradiation (Oró and Holzer, 1979) is more than an order of magnitude smaller than the measured rate of amino acid degradation by purely photolytic means (ten Kate, 2005). This is not to say that photochemical processes are unimportant. These three phenomena, H_2O_2 production from water vapour, frost-mediated O_2^- generation, and free oxygen attack, all contribute to the photochemical degradation of organic matter exposed to the atmosphere and lighting of Mars. The respective rates of destruction caused by these processes will vary depending on the locale considered and can occur in the absence of direct illumination. By contrast, UV photolysis is a global phenomenon wherever organic matter is exposed to direct sunlight, it can however be trivially prevented by a sub-micron thickness of an obscuring medium, such as the precipitation of airborne dust.

6 A simple weathering model

To provide a graphical interpretation of the above paragraph it is useful to construct a simplified model of the processes at work in a section of martian regolith. Mars' surface is host to a number of dynamic processes, as shown in the sketch of figure 1. Two of those phenomena, photolytic degradation and surface gardening will now be addressed. The exact form of the surface agitation is not treated rigorously, and is assumed to arise partly from background dust fallout, the disturbances of meteoritic impact, and dust-storm resurfacing. Consider a thin infinitesimal slice through a column of regolith, of total thickness Z . The regolith is assumed to have a uniform concentration of some organic material within in it. In the uppermost layer this organic contaminant is assumed to decay photolytically with a fixed half-life. From agitation and turnover, there is a probability, $P(z, \Delta t)$ that a layer at a depth z (and thus all of the material above it) will have a even chance of being disturbed in a time period of Δt . This can be written as,

$$P(z, \Delta t) = 1 - (0.5)^{\frac{\Delta t}{\tau}} \quad \text{Eq. 1}$$

Here, the half-life for the turn-over process, τ , varies with depth. Naturally, deeper layers are less frequently disturbed than overlying material and the scaling time of this process is assumed, in the absence of appropriate data, to be a power law, as;

$$\tau = T_0 z^{-k} \quad \text{Eq. 2}$$

Here, T_0 is the scaling duration for the disturbing process and the variable k determines the physical range of the agitation. As there are no direct clues for the values of T_0 or k , nominal values will be chosen for the

above equations such that two types of behaviour are shown in the model. Any action sufficiently vigorous to agitate a layer of regolith at some depth, such as a meteorite impact, is assumed to eject the overlying material which then settles back in an unsorted manner. This is modeled as an averaging procedure for all the material above the depth being considered.

Photolytic degradation is the process modeled here for removing organic matter and the effect of this is captured as a simple geometric relationship between surface concentration and exposure duration for the uppermost layer in the model. It is instructive to see how relatively small changes in the parameters governing overturn and degradation time result in very different depth profiles for the concentration of some hypothetical organic material. A Monte Carlo code using the above model has been written and executed. In figure 5a the index, k , which governs the physical depth to which gardening occurs, has a relatively small value; the sub-surface is then relatively static and the upper layer becomes progressively depleted with time. In figure 5b the model is run for the same amount of time, but here the gardening process has a deeper penetration (k has been trebled in value compared to 5a), and this leads to a more effectively homogenized regolith. Another result is that organic matter is present at higher concentrations at the surface than for the low k case, because the upper layer is disturbed before it can be totally cleansed of the simulated organic component.

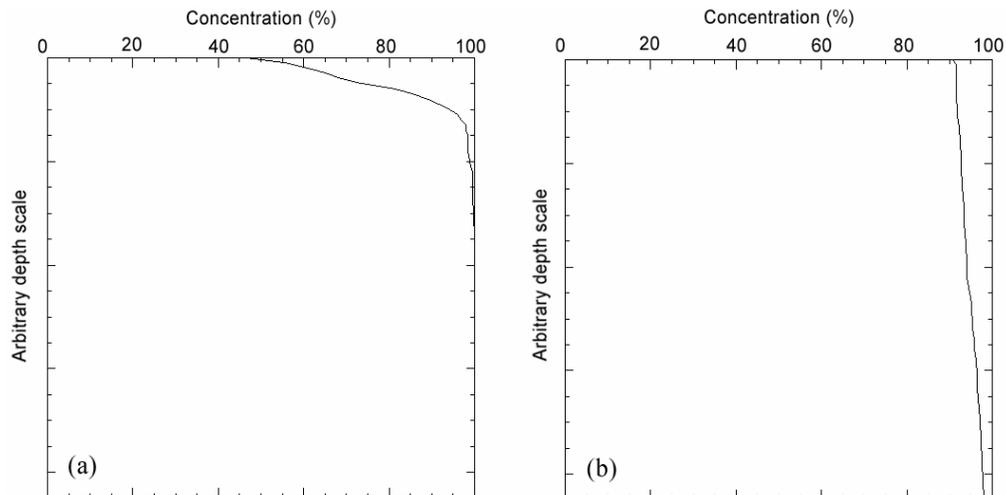


Figure 5a,b – Plots of concentration as a function of depth in a model regolith for different overturn constants.

Unfortunately, this type of modeling is plagued by many parameters that are poorly understood and less accurately modeled. There are at present no data for the transport and agitation of the martian regolith at the small scales considered, and the above example is given more as an illustrative guide than as an accurate example to be refined. However, it is instructive to consider how the great diversity of geological regions on Mars might lead, through selective dust deposition and abrasion, to areas that vary greatly in their ability to preserve organic matter.

Results and implications

The degradation of organic compounds at the surface of Mars has been examined piecemeal in numerous studies for almost thirty years. Partly, the inability to provide a single ‘smoking gun’ that explains the absence of native organic matter as seen by the Viking landers is a complex function of the limited sensitivity of the original apparatus and the probable complexity of the processes that compete to remove organic carbon from the martian environment. If organic matter is well shielded from the UV radiation that illuminates Mars’ surface, then that material can still be attacked by gaseous chemical species produced either by photochemistry of the atmosphere. Material cached in such a way so that they do not interact with diffusing species or light will be preserved in an essentially pristine state, and only revealed to the caustic surface UV and (presumed) photochemistry by the action of Aeolian abrasion.

Where organic material originating from meteoritic or hypothetical native sources is exposed to the martian surfaces it may to have a lifetime, via photolytic attack, that is considerably shorter than all but the briefest of surface phenomena that are able to transport a layer of dust, such as a Dust Devil. This possibility holds only if the preliminary studies discussed here are good models for the decay paths of more complex molecules. It is therefore possible that organic matter will not be found at Mars’ surface either exposed to the surface or loosely covered by an unconsolidated regolith layer.

Future Research

Mars still lies at the frontier of planetary science; a world very different to our own, but perhaps once having shared some of the unique features which have made Earth the sole known repository of life. In the coming decades increasingly sophisticated spacecraft, and it is hoped, eventually humans, will explore this world and in doing so help to answer the questions briefly examined in this chapter. An important adjunct to such work will be laboratory simulations of both past and present martian phenomena. The present desiccated and near-static state of the martian surface suggests the possibility of finding remnant traces of early chemical systems that might have flourished on Mars. This possibility brings with it a new realm of problems which are often described under the blanket term of ‘planetary protection’. For example, materials used in simulations of a sample-return mission would, for purposes of verifying the curation and dispersal procedures, need to be subject to the same protocols as a real extraterrestrial sample (Rummel, 2001). Thus, qualification materials with no detectable organic content would be needed and it is not clear as to how they might be made. Current spacecraft sterilization techniques (baking, gaseous oxidants, energetic radiations) are ineffective at removing organic matter, and rather than attempting to clean existing analogues, an inorganic synthesis route may be needed. Whatever process is devised for the production of both sterile and low-organic content analogues, such technologies and materials are common to the study of samples that are to be returned from Mars. The goals of laboratory studies are not the mere emulation of known processes, but the understanding of how photolytic and photochemical reactions depend on the environmental conditions of Mars, a complex and varied world. Although that planet’s past is lost to us, Mars present, and Mars yet to come, are places that we will come to know, and that

understanding will come about from further studies of how chemistry operates above, on, and in Mars surface.

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