New Paths for Survivability of Organic Material in the Martian Subsurface

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Key Point:

- environmental factors influence organic matter on Mars; our understanding of these processes evolves through lab studies of analog systems.

Abstract

Recent space missions have identified organics, chlorinated and non-chlorinated, on Mars. Understanding the origin, current state and reactivity of this carbonaceous material is critical to efforts to detect organic signatures of possible past life on Mars. Environmental effects such as UV radiation, pressure, diagenesis, aqueous activity and presence of perchlorates have been previously been assessed using analog experiments. To this list, Fox, et al. adds and quantifies the effect of galactic cosmic rays and solar winds on organic material on the surface and in the near sub-surface of Mars. Their work, using laboratory analog materials and radiation, shows that the same organic acids, formic and oxalic acid, are produced after exposure equivalent to that over Martian history at depths of less than 5 cm, independent of mineral matrix or starting organic materials. These experiments suggest that planned sub-surface exploration using the drill on the Rosalind Franklin Rover (ExoMars) will sample organic material which has not been altered by cosmic rays, although it may have been exposed to other environmental factors such as water or salts.

Plain Language Summary

One of the forthcoming missions to Mars, the Rosalind Franklin Rover (ExoMars), will have the capability to drill and sample the subsurface at depths of up to 2m. One of the goals of this missions, building on discoveries made by many previous missions, is to further our understanding of the organic material present on Mars and where it came from – that is, is it solely the expected material delivered by meteorites, or can it be evidence of possible past life on Mars? Using laboratory experiments, Fox et al. show that measurements made at depths deeper than 5 cm, well within the capability of the rover drill, will access organic material which has not been destroyed by cosmic rays. Their research also shows that it is impossible to unambiguously reconstruct the starting material from the products of radiation-mediated decomposition, emphasizing the need to locate unaltered material for study.

Commentary

The detection of organic molecules on Mars has been one of the grand challenges of solar system exploration since the Viking missions (Biemann et al., 1976). With the detection of hydrocarbons at Pahrump Hills and chlorinated hydrocarbons by SAM aboard MSL on Curiosity Rover at Gale Crater, the presence, although not the origin, of detectable quantities of organic material has been confirmed (Eigenbrode et al., 2018; Freissinet et al., 2015). The current challenge is to understand the sources and history of this material and the chemical changes it may have undergone since formation, with the intention of determining whether it is abiotic (i.e., meteoritic) or biotic. Another aspect of this challenge is understanding the transport and reactivity of these materials and their decomposition products to better predict where organic material might be found by ongoing and future missions and in what form it might be detected. Research in the last few years has begun to explore environmental influences on the preservation, alteration and destruction of organic matter on Mars using laboratory-based analog experiments.

The surface of Mars is an inimical place for organic molecules: along with being cold, dry, and airless, the soil contains strong oxidants such as perchlorates (Carrier et al., 2015) and the varied mineralogy offers different levels of preservation, all of which have been studied using laboratory analogs, summarized in Table 1. Organic material can also be selectively eliminated by the pressures and temperatures from asteroid impacts, which have occurred throughout Martian history and have been proposed as a natural drill for sampling the subsurface (Montgomery et al., 2016). Few of these environmental factors actively work to preserve organic materials, although some of them effectively do so by countering other, more destructive processes: e.g., water will wash away perchlorates detrimental to analyses, but also remove some organic material (Montgomery et al., 2019).

In addition, the surface of Mars is bombarded by radiation from space across a wide range of energies (Hassler et al., 2014; Pavlov et al., 2012). Due to the thin Martian atmosphere, the radiation which reaches the surface is far different from the radiation profile of Earth. Even if the exploratory focus shifts to sub-surface sampling, the effects of soil composition and the penetration of radiation through these different soils needs to be understood along with previously studied secondary processes such as aqueous alteration, fluid transport of organic material and shock pressures from impacts.

The effects of UV radiation have already been studied by Carrier et al., (2019) among others. In particular, only a few millimeters of rock are required to effectively shield organic molecules from UV effects. Their work showed that UV radiation penetrates common Martian minerals, especially gypsum, to deeper levels than previously thought, meaning that common meteoritic organic molecules (such as benzoic acid, phenanthrene, octadecane) have far shorter half-lives than previously estimated even under near (<4-5mm) subsurface conditions. Given the 2-meter depth capability of the Rosalind Franklin Rover drill, this is not an insurmountable obstacle.

However, there is another source of ionizing radiation on Mars which needs to be taken into account: galactic cosmic rays and solar winds, which are higher energy and penetrate up to 5 cm into the Martian surface. Cosmic rays are high-energy particles, primarily from outside the Solar System, which have sufficient power to cleave or otherwise react with organic molecules. On Earth, they react in the atmosphere and rarely reach the surface; Mars has no such protection (Pavlov et al., 2012). Fox et al., (2019) have used laboratory radiation on Martian analog materials to simulate the effect of cosmic rays and the solar wind on organic material at the surface or sub-surface of Mars.

Table 1: Analog Studies of Environmental Influences on Organic Materials in Natural Environments.

Environmental Influence	**Organic Material**	**Effect of environmental influence on organic matter**	**Reference**
Strong oxidants in soil	Type IV	Destruction during detection	Royle et al., 2018
Mineral Matrix	Natural analog	Varies	François et al., 2016; Lewis et al., 2018; Williams et al., 2019
Pressure & thermal shock (from impacts)	Types I-IV organic matter	Selective destruction	Montgomery et al., 2016
UV radiation	Synthetic meteoritic organic molecules	Destructive	Carrier et al., 2019 and references therein
Cosmic rays and solar wind	Kerogen, analog mixture	Produced organic acids	Fox et al., 2019

Fox et al., (2019) examined the effects of galactic and solar cosmic rays by exposing model combinations of organic matter and selected mineral matrices to radiation doses equivalent to geological time scales on Mars. By varying both the mineral matrices and the source of the organic material, they drew conclusions about the role of these rays in the destruction of organic material on Mars. Where breakdown products were detected, i.e., formic acid and oxalic acid detected as formate and oxalate respectively, they were produced in excess of any measured in the starting material, and they formed independently of the type of source organic material or mineral matrix. This suggests that detection of organic acids in Martian samples which have been exposed to radiation can only indicate the possible past presence of macromolecular organic material and provides no information about its origin.

The detected production of these organic acids does demand an explanatory mechanism. Previously, the production of organic acids due to UV radiation had been explained by Fenton chemistry (Benner et al., 2000). However, Fenton chemistry requires iron or other redox sensitive materials, which were not available in some of these cases. Fox et al., (2019) propose instead that organic acids were produced by radicals formed by semiconductor surfaces. Given the iron-rich nature of Mars, it seems likely that both mechanisms are at work there, and further work is needed to determine which mechanism is dominant in which location.

A third organic molecule, benzoic acid (detected as benzoate), was present in the initial organic samples, but declined in concentration after irradiation, showing that cosmic rays can also destroy organic acids, and that more complex feedback loops are possible. In the case of the fused silica matrix, the destruction was a straightforward linear relationship to increased radiation exposure. In the analog samples (olivine and clay, which could have acted as semiconductor surfaces), the relationship was much less clear, supporting the possibility of competing mechanisms.

With multiple missions to Mars underway, planned, or proposed, much work on analogs in the laboratory is needed for meaningful interpretation of the data expected in future from missions to (and possibly returning from) Mars. For example, Crandall et al., (2017) demonstrated the combined effect of cosmic rays on perchlorates to produce hydrogen peroxide (H_2O_2), which is even less amenable to preservation of organic material than perchlorate. One logical next step is to study of the effect of this excess H_2O_2 on organics over Martian geologic timescales, or on thermal decomposition analysis methods such as those used on existing and planned Mars rovers. As this body of laboratory analog studies grows, the next step will be further studies which look at the effects of multiple environmental factors acting in parallel and series. Such studies are needed to maximize understanding of precious Martian samples, whether studied in-situ on Mars, or on Earth in a future sample return mission.

As further information about planetary processes of Mars past and present is obtained, data from analog systems must also be taken into account to guide study site selection as well as to inform and comply with planetary protection guidelines ("The International Planetary Protection Handbook," 2019). The study by Fox et al., (2019) is a first step in understanding the radiation-driven alteration of complex organic matter on Mars. Recent laboratory-bench based studies of specific planetary processes suggest that the interplay between these planetary processes should be probed using further analog studies to ensure the best possible interpretations of forthcoming data from Mars.

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