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Influence of mineralogy on the preservation of amino acids under simulated Mars conditions

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ABSTRACT

The detection of organic molecules associated with life on Mars is one of the main goals of future life-searching missions such as the ESA-Roscosmos ExoMars and NASA 2020 mission. In this work we studied the preservation of 25 amino acids that were spiked onto the Mars-relevant minerals augite, enstatite, goethite, gypsum, hematite, jarosite, labradorite, montmorillonite, nontronite, olivine and saponite, and on basaltic lava under simulated Mars conditions. Simulations were performed using the Open University Mars Chamber, which mimicked the main aspects of the martian environment, such as temperature, UV radiation and atmospheric pressure. Quantification and enantiomeric separation of the amino acids were performed using gas-chromatography-mass spectrometry (GC–MS). Results show that no amino acids could be detected on the mineral samples spiked with 1 μM amino acid solution (0.1 μmol of amino acid per gram of mineral) subjected to simulation, possibly due to complete degradation of the amino acids and/or low extractability of the amino acids from the minerals. For higher amino acid concentrations, nontronite had the highest preservation rate in the experiments in which 50 μM spiking solution was used (5 μmol/g), while jarosite and gypsum had a higher preservation rate in the experiments in which 25 and 10 μM spiking solutions were used (2.5 and 1 μmol/g), respectively. Overall, the 3 smectite minerals (montmorillonite, saponite, nontronite) and the two sulfates (gypsum, jarosite) preserved the highest amino acid proportions. Our data suggest that clay minerals preserve amino acids due to their high surface areas and small pore sizes, whereas sulfates protect amino acids likely due to their opacity to UV radiation or by partial dissolution and crystallization and trapping of the amino acids. Minerals containing ferrous iron (such as augite, enstatite and basaltic lava) preserved the lowest amount of amino acids, which is explained by iron (II) catalyzed reactions with reactive oxygen species generated under Mars-like conditions. Olivine (forsterite) preserved more amino acids than the other non-clay silicates due to low or absent ferrous iron. Our results show that D- and L-amino acids are degraded at equal rates, and that there is a certain correlation between preservation/degradation of amino acids and their molecular structure: alkyl substitution in the α-carbon seem to contribute towards amino acid stability under UV radiation. These results contribute towards a better selection of sampling sites for the search of biomarkers on future life detection missions on the surface of Mars.

1. Introduction

The detection of organic molecules associated with extra-terrestrial life has been primarily focused on Mars due to its proximity to Earth, evidences of a congenial past environment and potential to support microbial life (Westall et al., 2013). Increasing evidence from NASA's *Opportunity* and *Curiosity* rovers obtained at different locations indicates that the Red Planet could have indeed supported life at the surface in the past (Arvidson et al., 2014; Grotzinger et al., 2014). Furthermore, the detection of silica-rich deposits by the Spirit rover in the Gusev crater is also an indication of an environment able to support life (Des Marais 2010; Ruff et al., 2011; Squyres et al., 2008). It is also plausible that life developed underground and biomarkers reached the surface (Michalski et al., 2013). Despite this, the environmental conditions that prevail now on Mars' surface are not congenial to life or to the preservation of biomarkers. Two of the factors contributing to the harsh current martian environmental conditions are the thin atmosphere and the absence of a significant magnetosphere (Fairén

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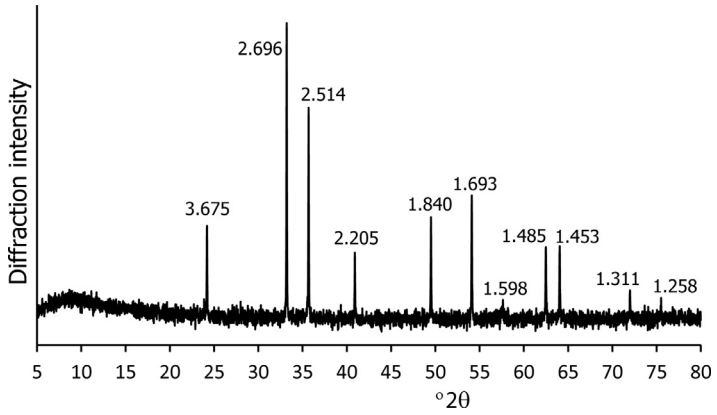

Fig. 1. Powder X-Ray diffraction patterns of hematite (Fe_2O_3). The figures indicate the d-spacing of the several peaks in angstroms. The intensity increase at ~10 °2θ is produced by the X-ray fluorescence of Fe.

et al., 2010), resulting in the inability to attenuate the intensity of the multiple forms of solar radiation that reach the planet, such as UV radiation, galactic cosmic rays and solar energetic particles (Cockell et al., 2000; Hassler et al., 2014). As a result, the martian regolith is exposed to intense levels of radiation, contributing to the reactivity of the soil which may destroy potential martian life and degrade organic molecules (Dartnell et al., 2007; Quinn et al., 2013). UV radiation leads to the formation of radical species (e.g. reactive oxygen species such as superoxide and hydroxyl radicals) by photochemical processes, which cause degradation of any potential organic compounds present on Mars (Benner et al., 2000; Georgiou et al., 2007, Georgiou et al., 2015; Yen et al., 2000). Amino acids, which are the building blocks of proteins and considered important target molecules in future life-searching missions (Parnell et al., 2007), are known to be subjected to degradation by UV radiation (Garry et al., 2006; Noblet et al., 2012). A 1.5-year exposure of glycine and serine to Mars-like surface UV radiation conditions in low-Earth orbit resulted in complete degradation of these organic molecules (Noblet et al., 2012).

In order to maximize the chances of finding biomarkers on Mars, we must determine the most suitable conditions to preserve them. Preservation of organic molecules on Mars is thought to be favored in subsurface environments, and also through associations with specific minerals that may confer protection from the harsh surface conditions (Kminek and Bada, 2006; Summons et al., 2011, and references therein; Poch et al., 2015). Despite the unfavorable conditions that are found at the surface, indigenous chlorinated hydrocarbons were recently detected on Mars by the Sample Analysis at Mars (SAM) instrument on-board Curiosity (Freissinet et al., 2015). The successful detection of organic molecules on samples from Mars' surface exposed to ionizing radiation and oxidative conditions suggests that: 1) the preservation of organic molecules may not be limited to subsurface environments, and 2) organic biomarkers may be found on the surface if associated with specific minerals.

In this paper we examine the preservation under simulated Mars-like conditions of amino acids that were spiked onto 11 minerals and onto basaltic lava, which are all present on the martian surface (Ehlmann and Edwards, 2014). The simulations were performed using a custom-built Mars environmental simulation chamber at the Open University (OU), Milton Keynes, UK. This facility permits multiple aspects of the martian environment to be simulated, including temperature, UV radiation, atmospheric pressure and composition. Analyses of the amino acids extracted from the mineral surfaces after the experiments were performed by gas chromatography-mass spectrometry (GC-MS). Our results are particularly relevant for future in situ life-detection missions, such as the ESA-Roscosmos ExoMars 2018 rover and the NASA Mars 2020 mission, highlighting which minerals may be the most suitable to protect amino acids from the harsh environmental conditions found at the martian surface.

2. Materials and methods

2.1. Minerals and XRD characterization

Eleven mineral samples were used in this work: augite (A), enstatite (E), goethite (G), gypsum (Gy), hematite (H), jarosite (J), labradorite (L), montmorillonite (M), nontronite (N), olivine (O) and saponite (S). Basaltic lava (B) was also used. They were all selected as representing abundant mineral phases on Mars (Ehlmann and Edwards, 2014). Augite, jarosite, labradorite, nontronite, and saponite were purchased from Richard Tayler (http://richardtayler.co.uk, Cobham, Surrey, UK). Enstatite, goethite and olivine were obtained from the Natural History Museum collection (NHM, London), all of them unregistered specimens in the NHM collection. The basaltic lava is a specimen collected in Mauna Loa (Hawaii) at the point of lava quenching and donated by Joe Michalski. Gypsum and hematite were purchased from Sigma Aldrich. The montmorillonite is SAz-1 (smectite-rich rock of volcanic origin) described in Cuadros (2002).

Minerals were ground to powder by hand with a mortar and pestle and they were analyzed with X-ray diffraction (XRD) at the NHM, in order to determine their purity and structure. They were side-loaded to avoid preferred orientation of particles and analyzed in the range 3–80° 2θ using a PANanalytical X'Pert Pro diffractometer operated at 45 kV and 40 mA, with Cu Kα radiation, divergence slit of 0.25°, Soller slits of 1.146° and a solid-state X'Celerator detector covering an angle of 2.1°. The basaltic lava contains the following mineral phases in the estimated order of abundance: volcanic glass, pyroxene, olivine, and labradorite. Jarosite is of the natrojarosite variety. Olivine is forsterite. The augite and enstatite contain some traces of amphibole; the nontronite and montmorillonite contain traces of quartz; the other minerals are pure at the XRD detection level. Fig. 1 shows the X-ray pattern of hematite as an example.

2.2. Chemicals and tools

The pipette tips and eppendorfs used in this work were bought sterile. Hydrochloric acid (37 wt. %), and high performance liquid chromatography (HPLC)-grade water were purchased from Sigma-Aldrich. Sodium hydroxide was purchased from Riedel-de Haen. Aluminium hydroxide and 2-aminoheptanoic acid (>97%) were purchased from Fluka. AG 50W-X8 resin (100–200 mesh) was acquired from Bio-Rad. HPLC-grade dichloromethane (DCM) was