

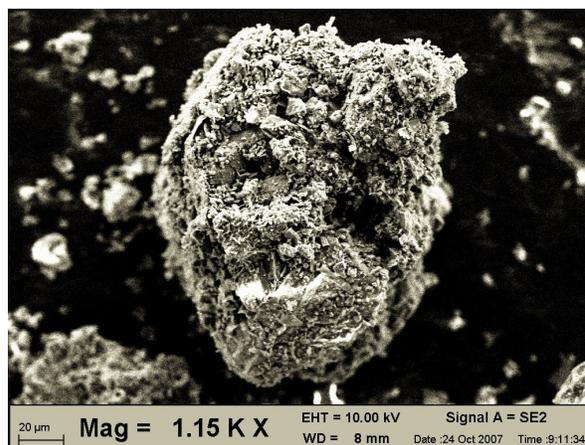
**MARS REGOLITH ANALOGUES – INTERACTIONS BETWEEN MINERALOGICAL AND ORGANIC COMPOUNDS:** Z. Peeters<sup>1</sup>, R. Quinn<sup>2</sup>, Z. Martins<sup>3</sup>, L. Becker<sup>4</sup>, J. Brucato<sup>5</sup>, P. Willis<sup>6</sup>, F. Grunthaler<sup>6</sup> and P. Ehrenfreund<sup>1</sup>, <sup>1</sup>Leiden Institute of Chemistry, Einsteinweg 55, 2333 CC, Leiden, the Netherlands, z.peeters@chem.leidenuniv.nl, <sup>2</sup>SETI Institute, NASA Ames Research Center, Moffett Field, CA 94035, USA, <sup>3</sup>Dept. of Earth Science and Engineering, Imperial College London, London SW7 2AZ, UK, <sup>4</sup>Univ. Calif. Santa Barbara, Dept. Geol. Sci, Inst. Crustal Studies, Santa Barbara, CA 93106, USA, <sup>5</sup>Istituto Nazionale di Astrofisica, Osservatorio Astronomico di Capodimonte, via Moiariello 16, 80131 Napoli, Italy, <sup>6</sup>In Situ Exploration Technology Group, NASA Jet Propulsion Laboratory, Pasadena, CA, USA

**Introduction:** We describe investigations of the physical and chemical properties of Mars soil analogues and the influence of the mineralogical matrix on the stability of amino acids. We collected soil samples from the Atacama desert near the Arequipa region in Peru and near the Yungay region in Chile. We measured the pH, redox potential, ion concentrations, elemental composition and carbonaceous compounds of various desert samples. The results show large differences for the measured properties, even for samples taken only several metres apart. Desert soil samples were exposed to a simulated Mars environment to test the stability of amino acids. The results show high levels of amino acid destruction. From our results we conclude that the amino acid stability in the desert soil is influenced by the mineralogical composition of the samples.

**Experimental:** Oxidation-reduction potential ( $E_H$ ) and pH measurements were taken using an Orion 635 MMS™ Meter with an Orion 61-79 pHuture™ combination Quatrode™ (pH/ORP/temperature) electrode with Orion pHuture Sure-Flow Reference Probe Filling Solution (610011). Elemental composition of the soil samples were measured with EDX spectroscopy. Individual grains of each desert soil sample were analysed by field emission scanning electron microscopy (FESEM). A Bruker IFS66v interferometer was used to obtain infrared laboratory spectra. The stability of amino acids in the selected martian soil analogues was tested in a set-up built for this purpose, described in [1]. The Mars simulation experiments were conducted in a diurnal cyclic mode, starting with 12 h of irradiation, followed by 12 h of cooling to -60 °C. Each experiment lasted 4 diurnal cycles, equivalent to 4 martian sols. The Mars simulation chamber contained <14 ppm water during the experiment (water vapour varies in the martian atmosphere, between 10–1000 ppm [2]). To test the degradative capacity of the desert soils the amino acid content was measured before and after 4 diurnal cycles in the Mars simulation setup by HPLC–FD via OPA/NAC derivatization [3].

**Results:** FESEM analyses exhibit morphologies recalling a porous structure coating grains of sample TOS2005 from the Arequipa region (see Figure 1). Sands with micron-size grains are trapped forming cushion-like pellets shaping the soil beneath.

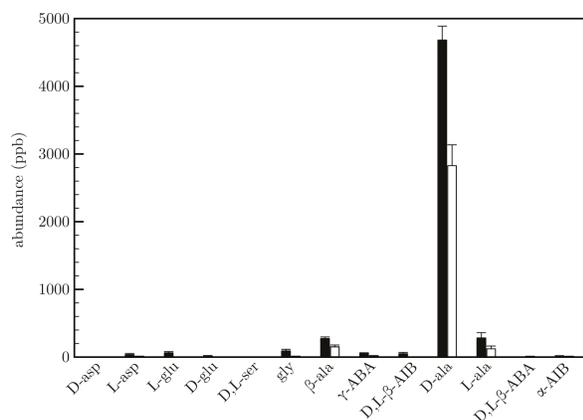
Highly porous structure retains water better favouring the activation of dried micro-organisms.



**Figure 1.** Field emission scanning electron microscopy (FESEM) picture of sample TOS2005 (FROM THE Arequipa region). Electrons were accelerated to 10 kV.

The reflectance spectrum of TOS2005 resembles those of andesitic rocks. Anorthite is the dominating mineral observed in most of the Atacama desert samples.

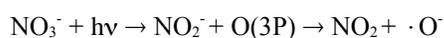
*Mars simulation experiments.* Abundances of the amino acids present in the desert soil samples were determined before the Mars simulation experiments were conducted and showed low amino acid abundances of a few ppb. Sample TOS2005 was therefore spiked with 4.5 ppm D-alanine before exposure to simulated Mars conditions. After exposure, amino acid abundances were determined using HPLC–FD [3]. Figure 2 shows the resulting abundances (white bars), along with the abundances of the non-exposed sample (black bars). Most amino acids showed a much lower abundance after exposure to the simulated Mars environment. A decrease of ~85 % was observed for most amino acids. Of the 4.5 ppm D-alanine that were added to the soil before exposure 2.7 ppm were recovered, a difference of 40 %.



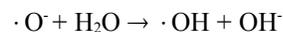
**Figure 2.** Amino acid abundances in TOS2005 (Arequipa soil sample) spiked with D-alanine. Black bars give the abundance before exposure to a simulated Mars environment and the white bars after exposure. The error bars denote the standard error of the mean.

**Discussion:** Parts of the Atacama desert are among the driest places on Earth. For this reason, the soils in these desert regions have been used as an analogue for the regolith of Mars [4]. Besides being extremely dry, the martian regolith is also depleted in most organic compounds above ppb levels, as inferred from the Viking data [5]. From our results it is clear that the Arequipa and Yungay soils (Atacama desert) are largely devoid of amino acids. We have tested the stability of amino acids in soil samples from the Arequipa region (TOS2005). Because of the low abundance of amino acids in that sample, the soil was spiked with D-alanine before exposure to a simulated Mars environment. The results in Figure 2 show a decrease in amino acid abundance for the Arequipa soil. Degradation of amino acids directly by UV radiation is possible [6], but UV radiation will be attenuated by the first layer of soil grains it encounters. Direct degradation by UV radiation would therefore only photolyse the amino acids that are located on top of the soil grains and a destruction of only a few % would be the result. However, Figure 2 shows that the loss of amino acid is much larger for the Arequipa sample, which implies that additional mechanisms for degradation are active.

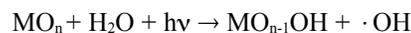
TOS2005 displayed in Figure 2 contains 64 ppm  $\text{NO}_3^-$ . When the samples are irradiated, photoactivation of nitrate can occur.



When water condenses or absorbs onto the samples, the oxide radical can react with water to form an OH radical.



Similar reactions can occur with metal oxides present in the soil.



In combination with iron bearing minerals, UV radiation may initiate a photon-enhanced Fenton-type (photo-Fenton) reaction. Radicals produced in the above reactions can oxidize the amino acids in the soil, leading to their destruction. The production of radicals and the degradation of amino acids are therefore dependent on the mineralogical composition of the soil.

Testing the physical and chemical properties of Mars regolith analogues such as pH, redox potential, elemental composition, ion concentrations, conductivity, the organic content, and more specifically the amino acid abundance is an important tool in the framework of life detection. Our results show that samples which are located in close vicinity (separated by only a few metres) can vary strongly in chemical and physical properties. The mineralogical composition of the soil strongly influences the stability (or destruction) of the amino acids and other organic compounds. It is therefore important that future missions to Mars consider the complex interactions between organic compounds and the mineralogy of a proposed landing site, to increase the chance of finding organic molecules on Mars.

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