LIFE DETECTION AND ORGANIC CHARACTERIZATION IN THE SOLAR SYSTEM. H-S. Chan[1], Z. Martins[1] and M. A. Sephton[1], [1]Department of Earth Science and Engineering, Imperial College London, UK (z.martins@imperial.ac.uk).

Introduction: Life on Earth may not be unique in our Solar System. One of the most likely extraterrestrial host for life is our planetary neighbour Mars. In the forthcoming decade ESA and NASA will launch several missions to the Red Planet to search for any signs of past or present life. One of the instruments previously proposed to be on board in one of these space missions contained a laser-induced fluorescence (LIF) detector [1]. This is able to detect organic molecules that may be present on the Martian regolith, in particular amino acids, polycyclic aromatic hydrocarbons (PAHs), and nucleobases. Amino acids are crucial molecules because they are the building blocks of proteins and thus have an implication for the origin of life. Insights into what organic responses detected on Mars mean about the presence of life can only be provided by studying similar responses from Mars like Earth rocks. Therefore the study of Mars soil analogues is a pre-requisite for successful space missions. Soil samples collected in Salten Skov (Denmark) have been recognized as one of the various analogues that can resemble the Martian soil [2-7]. Several studies have investigated their mineralogical and magnetic properties [2-4,6], but thorough chemical studies have not yet been done [5,7]. Therefore, we have performed fluorescence spectroscopy analysis of the solvent-soluble amino acid fraction of the Salten Skov soil, and the results were compared to typical laboratory analysis (e.g. HPLC-FD and GC-MS).

Experimental Section: Amino acid extraction and desalting procedure was performed on the clay size fraction (<63 μm) of the Salten Skov soil based on the method by [8,9]. The soil extracts were then analysed by fluorescence spectroscopy. 10 μl (out of 100 μl) of the soil sample extract, 900 μl of 0.1% (w/v) fluorescamine in acetonitrile, and 150 μl $Na_2B_4O_7{\cdot}H_2O$ were placed in silica cuvettes (light path 10 mm). Water was added to a final volume of 3 ml. The sample was given a reaction time of 5 minutes before being analyzed with the Horiba Jobin Yvon FluoroMax-4 spectrofluorometer, using an excitation wavelength of 390 nm. A control blank was heated to 500°C for 3 hours and went through all the same experimental procedure as the soil sample.The blank solution was measured and subtracted from the soil sample spectra. All the data was compared to amino acid standard solution composed of mixtures of 17 different amino acid standards (i.e. D,L-alanine, D,L-aspartic acid, EACA, D,L-glutamic acid, glycine, D,L-leucine, D,L-norleucine, D,L-norvaline, D,L-serine, D,L-valine, D,L-α-ABA, α-AIB, D,L-isovaline, D,L-β-ABA, D,L-β-AIB, β-alanine and γ-ABA).

Results and Discussion: The excitation wavelength for individual amino acid standard solutions was optimized and identified to be 390 nm. This generates the highest fluorescence intensity (maximum emission wavelength around 480 nm) across individual amino acid standards as well as amino acid standard mixtures The emission spectra of various amino acid standards mixture are shown in Figure 1.

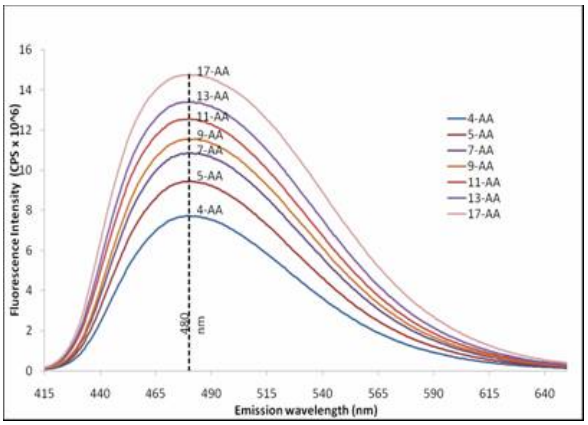

Figure 1. Emission spectra of 4- to 17-amino acid standard mixtures (blank-corrected) using the optimized excitation wavelength of 390 nm. 480 nm was found to be the maximum emission wavelength for amino acids.

The measured fluorescence intensities of the amino acid standard mixtures are significantly lower than the estimated intensities (i.e. sum of the individual amino acid emission spectrum). This indicates that photochemical quenching occurs to higher order amino acids mixtures, causing a decrease in the fluorescence emission from 1.4 times (in the 2-amino acid standard mixtures) to 2.4 times (in the 17-amino acid standard mixture). This is in agreement with the fact that when the amino acid standard solution is more concentrated, the intermolecular interactions become more prominent, which therefore contributes to increase the quenching ratio.

The amino acid content of the Salten Skov soil has been analysed by fluorescence detection (Figure 2). The maximum fluorescence intensity of the hydrolysed Salten Skov solution is approximately 3.85×10^6 CPS, meaning that there is a high amino acid content present in the sample. However, the intensity of the hydrolysed

Salten Skov samples is 76% lower than the non-hydrolysed fraction (Figure 2). This is explained by the fact that the hydrolysed fraction contains the total amino acid content (free plus bond), while the non-hydrolysed fraction contains only free amino acids. Therefore, a higher amino acid content in the hydrolysed fraction leads to higher quenching.

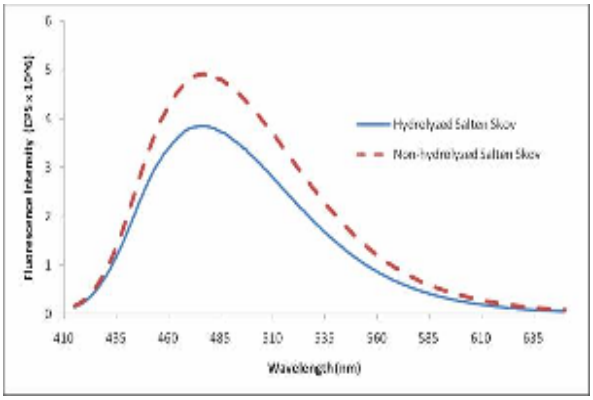

Figure 2. Emission spectra (blank corrected) of the hydrolysed and non-hydrolysed fractions of the Salten Skov soil, using an excitation wavelength of 390nm.

Previous analysis of the amino acid content of the Salten Skov soil using HPLC-FD and GC-MS showed that the most abundant amino acids are L-aspartic acid, L-glutamic acid, glycine, L-alanine and serine [5,7]. An amino acid standard solution prepared with these five amino acids (and with total amino acid concentration in the same range as the Salten Skov total amino acid concentration) was analysed by fluorescence spectroscopy and compared to the emission spectra of the Salten Skov soil. The fluorescence spectra of the Salten Skov soil and the 5-amino acid standard solution are similar, both in shape and in the maximum emission wavelength.

The ultimate goal of these fluorescence spectroscopy analyses is to enable the identification of multiple amino acid mixtures on the surface of Mars. Because soils containing organic molecules often contain a heterogeneous mixture, one must be able to deduce the identity and concentrations of multiple compounds from a single fluorescence spectrum. However, our results show that different amino acid mixtures have maximum emission at similar wavelengths, making definitive identification of individual amino acids difficult. Despite this, fluorescence spectroscopy offers a number of important capabilities. The technique is non-invasive and non-destructive. Although definitive elucidation of exact concentrations and identifications of multiple amino acid mixtures within a heterogeneous soil will be difficult to achieve, it will be possible to distinguish these from other organic molecules such as PAHs and nucleobases [10]. For example, PAHs do not produce an emission spectra when excited with an excitation wavelength of 390nm. Instead, the excitation wavelength should be set to 290 nm in order to be able to detect any PAH mixture [10]. Such capability represents a significant contribution in the characterization of the martian organic chemistry, and in the detection of any signs of life in the Red Planet.

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