ANTARCTIC ANALOGUES FOR MARS EXPLORATION: A RAMAN SPECTROSCOPIC STUDY OF BIOGEOLOGICAL SIGNATURES.

Howell G..M. Edwards[1], Caroline A. Moody , Susana E. Jorge Villar[1,2] and the late David D. Wynn-Williams[3]

[1] Department of Chemical and Forensic Sciences, University of Bradford, Bradford BD7 1DP, UK.
e-mail: h.g.m.edwards@bradford.ac.uk

[2] Area de Geodinamica Interna, Facultad de Humanidades y Educacion, University of Burgos, Calle Villadiego S/N, 09001 Burgos, Spain.

[3] Antarctic Astrobiology , British Antarctic Survey , High Cross , Madingley Road , Cambridge CB3 0ET , UK.

Introduction: The present conditions at the surface of Mars are not conducive to the survival of life forms, with the thin atmosphere, lack of water, a highly-oxidising regolith and significant UV insolation. The Antarctic provides a terrestrial model with a transect from the maritime, where epilithic colonies can survive through the production of protectant biochemicals, to endolithic systems at the "limits of life" where existence at the surface is impossible [1,2] . In the Antarctic Dry Valleys, the extremely low humidity coupled with low temperatures reaching - 35°C, strong katabatic winds blowing from the Polar plateau and intense UV-radiation exacerbated by atmospheric ozone depletion at higher latitudes provides a putative analogue for the hostile conditions that life must tolerate for survival at or near the Martian surface [3,4].

This extreme terrestrial ecosystem is believed to mirror the conditions under which the evolution of organisms would have had to adapt to the steadily worsening environmental situation on Mars , as exemplified by Epochs III and IV , which effectively describe the Martian surface , subsurface and atmosphere over the last 1.5 million years [4 ,5].]The surface temperatures on Mars range from $-123\ ^0$C to $+ 25\ ^0$C, it's atmosphere is thin and transmits UVB and UVC radiation , and the presence of liquid water at the planetary surface is still conjectural. Clearly , the identification of Antarctic microniches which are amenable to analytical study can provide suitable examples of extremophile terrestrial behaviour of direct relevance to Mars.

Antarctic extremophiles : Special strategies are vital for the adaptation of Antarctic lichens and cyanobacteria to these extreme conditions [6,7]; in addition, the Antarctic provides a gradual change in ecosystem tolerance along a transect from the relatively milder maritime conditions experienced at the coast through to the cryptoendoliths , which are effectively the most adaptable colonies in the Polar region, after which only fossil cyanobacterial evidence is found at the highest latitudes [8,9]. This means that the different strategies being enforced for the survival of these organisms under worsening environmental habitats can be exploredexperimentally and evaluated analytically to assist the predictions of response of organisms to extremes of stress.

To reduce the amount of UVB and UVC radiation reaching the organisms , it is essential that the colonies produce a suite of radiation-protective chemicals for filtering out the low-wavelengths whilst still maintaining their capability for accessing the photosynthetically active wavelengths required for their metabolic processes [10,11]. Hence, it is possible to identify as protective biomolecules complex organic chemicals such as beta-carotene and a range of pigments such as parietin , rhizocarpic acid and calycin --- the former is believed to act as a UV –filter and also function in a DNA-repair mechanism for cell damage caused through radiation exposure, whilst the latter pigments are thought to behave as accessory radiation protectants [11,12,13] . We have carried out some experiments over a two-year period on Antarctic colonies which have been subjected to full radiation exposure at Jane Col , Leonie Island , compared with other colonies at the same site which have been shielded by UVB- and UVC–absorbent plastic cloches. Using nondestructive Raman techniques, it is possible to monitor the production of pigments in response to changes in the environmental situation---in particular , the relative proportions of parietin and beta-carotene in protected and unprotected colonies indicates a possible dualistic role for these pigments [14,15].

The production of hydrated calcium oxalates by colonies under stress is also a key factor of change in other circumstances ; it has been suggested that these oxalates are produced as chelators of heavy metals in the substrate, as water storage devices , acidity controllers and as anti-herbivoral agents. We have recently found evidence for the biogeological modification of iron oxides by extremophilic colonies in the most highly stressed conditions . The importance of this is two-fold , since it not only provides another parameter of knowledge for the understanding of the mechanisms by which terrestrial organisms survive these extremes , but it also gives a clue as to the sort of biogeological changes that have been effected by extremophilic organisms at the limits of life. Hence, in a situation , such as that which probably applied on Mars , any vestiges of extremophilic life would be incapable of tolerating or adapting to the worsening conditions, and they would pass into the fossil record. The clues to their former existence would then be totally found in the geological record and in a suite of unusual relict chemical compounds found there.

Raman spectroscopy : The viability of Raman spectroscopy to identify the key spectral biomarkers of extinct or extant life in the biogeological record has been amply demonstrated for the analysis of Antarctic endoliths [16,17] . The Raman biosignatures of key protectant molecules have been established for the identification of the strategies adopted by cyanobacteria for the colonisation of geological strata . An important requirement here is the ability of the analytical spectroscopic tecnique employed to locate and identify the key biomarkers in the geological systems that might be expected to be encountered in planetary exploration.

The miniaturisation of laboratory-based Raman spectrometers to a size which makes them suitable for part of an instrumentation suite on a robotic lander on a planetary surface has been receiving much attention recently [17-19]. Clearly, the evaluation of prototype instruments for Martian surface or subsurface exploration would be well served by analytical experiments involving Antarctic materials.

In this paper we shall discuss the comparative data obtained from several Raman instruments on Antarctic extremophiles which will include an epilith from Signy Island, a chasmolith from the Lake Hoare LTER site in the Dry Valleys , a cyanobacterial mat from Lake Vanda and an endolith from Mars Oasis (this latter specimen must be considered to be especially relevant to planet Mars !). Some of the advantages of the Raman technique for adoption as analytical instrumentation on a mission to Mars will emerge from this study.

In particular , the capability of the Raman technique for the identification of the spectral biomarkers under different conditions , without special sample preparation and in a micro-sampling mode , giving a specimen “footprint” of only several microns diameter is assessed . A critical factor in this series of experiments is the wavelength selection of the laser excitation employed for the analysis and information from spectra recorded with visible and near-infrared laser sources [20] . This information is relevant for the design of miniaturised Raman instruments that will have the objective of searching for extant or extinct life on planetary surfaces or subsurfaces, especially Mars.

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