PREPARATIONS FOR THE LAUNCH OF THE EXOMARS RAMAN LASER SPECTROMETER – A REVIEW OF RECENT STUDIES WHICH HIGHLIGHT THE ASTROBIOLOGICAL & GEOLOGICAL CAPABILITIES OF PORTABLE RAMAN INSTRUMENTATION. I. B. Hutchinson1, H.G.M. Edwards1, R. Ingle1, L. Harris1, M. McHugh1, C. Malherbe1, J. Jehlicka2, C. Marshall3 & J. Parnell4, 1University of Leicester, University Road, Leicester, UK. 2Charles University in Prague, Institute of Geochemistry, Mineralogy and Mineral Resources, Albertov 6, 12843 Prague, Czech Republic. 3Department of Geology, University of Kansas, Lawrence, Kansas, USA. 4University of Aberdeen, King’s College, UK. *ibh1@le.ac.uk

Introduction: The ExoMars rover, which will be launched in 2018, will carry a small analytical laboratory that will be used to study samples extracted from the Martian surface and sub-surface (up to 2m in depth). The laboratory will make use of an infrared spectrometer (and imager), a molecular analyser (mass spectrometer) and the first Raman instrument to be deployed on the surface of another planet [1] in order to analyse crushed samples generated by the ExoMars Sample Preparation and Distribution System (SPDS). The Raman Laser Spectrometer (RLS) will provide a spectral resolution of < 10 cm⁻¹ across its 200-3800 cm⁻¹ spectral range and will incorporate a 532 nm laser, a holographic transmission grating and a very sensitive, back-illuminated CCD detector [2]. A non-imaging optical head unit will produce a 50μm excitation spot on the surface of the sample and will collect (and filter) the scattered light and Raman emission from the crushed material.

Raman spectroscopy is recognized to be a powerful analytical technique that is sensitive to both organic and inorganic molecules/molecular ions. When operated at appropriate power levels (i.e. spot sizes), the measurement process is non-destructive and therefore it will be possible to perform a thorough analysis of all samples collected during the mission before subsets have to be selected for destructive testing.

In order to survive in some of the harshest known terrestrial environments (e.g. extremes of temperature, chemical toxicity or intense UV radiation), organisms produce a range of protective chemicals and modify their immediate environment in the process. The interaction between the host material and the organisms is critical for successful colonisation and the biological modification of the geological matrix plays a significant role in the organism’s ability to survive. Clear identification of the unique spectroscopic signatures associated with these chemicals/processes is an important step towards confirming the presence of extinct or extant life (either in a terrestrial or extraterrestrial environment) and it is important to ensure that appropriate databases of these signatures have been collected and thoroughly analysed before launch (using instrumentation and operating modes that are representative of the flight instrument).

Overview: A number of proto-type systems have been developed by members of the RLS consortium in order to prepare for mission operations and to optimize/demonstrate the capabilities of the component parts of the instrument [3][4]. Here we provide a review of recent sample testing programmes performed with a flight-like system which was developed to enable testing and optimisation of the flight detector/camera system as well as portable spectrometers which are similar in design and performance to the systems that have been proposed for planetary exploration. Spectra have been acquired from a number of analogue and real world samples using flight representative operating modes and environmental conditions and the advantages of using Raman spectroscopy for the recognition of some key molecular biosignatures is highlighted.

Sample Studies: A wide range of analogue samples have been used during the prototype test programmes. These include both: extremophile samples that contain biological signatures [3] and basalts/cherts [5][6] that contain degraded forms of carbon. A number of the samples were crushed before testing in order to replicate the SPDS process that will be implemented by the ExoMars rover [7]. We report on results obtained from a number of these studies both in terms of the overall instrument performance and the implications for the selection of appropriate (optimised) operating modes and on-surface experimental procedures. In particular, we present data which illustrates the changes in spectral response that result from the crushing of the materials and compare the spectra obtained to those acquired from whole specimens.

Carbon
Several carbon containing samples have been analysed with the portable instruments [e.g. 5, 6]. Data from these studies have demonstrated that the systems are able to identify/distinguish between separate sources of carbon (within the same sample) and are sensitive to concentration levels as low as 0.01% - 0.05% (depending on the particular sampling mode adopted and the grain size distribution of the crushed material) in reasonable agreement with studies elsewhere [8]. Detailed analysis of the positions and widths of the carbon D & G bands also enables information on the thermal maturity of the samples to be inferred – e.g. [6][9][10][11].

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**Gypsum crust**

Several samples of naturally occurring gypsum crust colonized by halophiles (i.e. samples containing microbrial pigments in three separate layers) were obtained from salterns at Eilat and were analysed with the prototype system (see spectra in Fig. 1). The data illustrate the capability of the instrument design to distinguish between the signals associated with the different layers using total acquisition times of less than 60 seconds.

![Figure 1: Example carotenoid spectra obtained from halophilic archaea and bacteria living in a geological substrate (acquired using the detector prototype system with integration times in the range 5-60s) [courtesy of McHugh 2013].](image)

**Desert Varnish**

Several rock specimens exhibiting a varnished surface were obtained from various locations in Death Valley, USA [courtesy Carr A. & Boom A.]. Desert varnish, also known as rock varnish or desert patina, is a thin skin, often only microns in thickness, comprising iron (III) oxides, manganese (IV) oxides and clays found on the outer surfaces of rocks in hot and cold desert environments [12]. The first suggestion that desert varnish might have a biological origin was made independently by White and Laudermilk [13][14] who postulated that botryoidal nucleation could arise from epilithic manganese-oxidising bacteria, fungi and algae in desert conditions. Astrobiological relevance of desert varnish to the search for life on Mars can be referenced to the detection of biological components in the mineralogical matrix [15] and to the visual observation of rocks at the NASA Mars Pathfinder mission landing site [16]. These samples provide an ideal range and variety of Raman signatures with which to demonstrate the overall performance and capabilities of the portable instruments. The spectra presented in Fig. 2 were acquired from multiple locations on one of the samples with a low power, (non-imaging) portable spectrometer and highlight the presence (and ability to detect) of various components in the specimen.

![Figure 2: Raman spectra acquired from various positions on the varnish (the laser wavelength was 785 nm and the integration time was 20s) [courtesy of Malherbe 2014].](image)

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