HIGH RESOLUTION ANALYSIS OF SELECTED ORGANIC COMPOUNDS IN ICY TERRAINS, USING SURFACE-ENHANCED RAMAN SPECTROSCOPY.

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Introduction: Raman Spectroscopy in Planetary Exploration: Studies using conventional laser Raman instruments have made a good case for application of this type of spectroscopy to planetary exploration. The detection of pigments sited in microbial matter in a range of samples from extreme environments (e.g. [1]) has supported development of the technique for space exploration generally, and Mars exploration in particular [2]. A major advantage of conventional Raman spectroscopy is that it can be applied to simultaneous characterization of bond types in both organic and inorganic materials.

The characterization of the organic component of a sample by Raman spectroscopy is best achieved when the technique is applied in a microscopy format, and the organic analyte analysed separately to the mineral matrix. Analyses can easily be repeated, adjusting the spot size and depth of focus until a good quality spectrum is obtained. This is the approach commonly taken when applying the technique to carbonaceous chondrites for example. Data with a high spectral resolution can be built up and specific spectral features mapped. In this way a skilled user can visually sort through an image and target components of interest. The automated collection of data in a spatial context is very powerful and can identify structures that may be of biological origin [3].

However, if not applied in a microscopy format Raman spectroscopy has a much lower resolution for minor and trace organic compounds. Firstly, a probe (a quick measurement not made via a microscope) contacting the surface of a geological sample will record spectra pertaining to the bulk mineralogy and not the trace organic components (e.g. organic analytes). Secondly, extracts of geological materials comprise a complex mixture of organic compounds that fluoresce, which greatly inhibits identification of spectral characteristics (Fig. 1). Thus the detection of polycyclic aromatic hydrocarbons within sea water, an assay format for which Raman Spectroscopy is commonly cited as a reliable first responder technique, can be complicated by fluorescence inherent to the sample.

Surface-Enhanced Raman Spectroscopy (SERS): Surface-Enhanced Raman Spectroscopy (SERS) increases the sensitivity by several orders of magnitude, and has been shown to overcome the problems created by the fluorescence of natural materials ([4]; see Fig 1). SERS is achieved by adsorbing the target analyte onto the surface of a metal. This usually requires an extra stage of sample processing, but it can be performed in a microfludic format. We are combining the additional sample processing necessary for SERS with sample preparation also performed in a microfluidic format (including extraction and sample concentration). The final result will be a very rapid assay, capable of detecting ppb concentrations of certain organic analytes. We demonstrate the value of SERS through application to detection of organic molecules in samples from an icy terrain. This has strong astrobiological relevance as the Martian polar regions are regarded as a prospective target in the search for life [5].

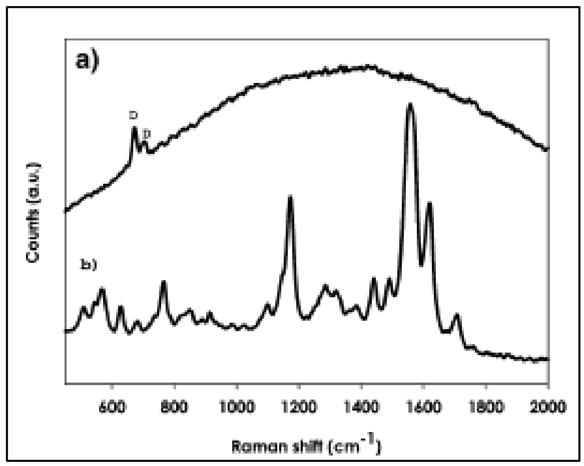

Fig. 1. Spectra obtained for 100 micromolar concentration solution of pigment scytonemin. a) Raman Spectrum, illustrating fluorescence and b) Surface Enhanced Raman Spectrum acquired in presence of silver colloid showing enhanced peaks for scytonemin. Laser wavelength 532 nm; power 10 mW.

Snow algae: Snow algae are extremophiles that live and grow in semi-permanent to permanent snow or ice in the alpine or polar regions of the world. In the U.K. they are found in old (semi-permanent) snow beds on the northern side of the Cairngorm plateau, Scotland. Their optimum growth temperature is below 10ºC. To survive in this extreme environment they require several adaptations. These include the biosynthesis of pigments, polyols, sugars and lipids, mucilage sheaths, motile stages and spore formation [6]. Pigments include carotenoids and chlorophyll [7]. Pigments are especially amenable to detection using Raman spectroscopy, and the characterization of snow algae using conventional Raman spectroscopy has been demonstrated in support of astrobiological exploration [8]. Snow beds are a good target for the detection of life since snow algae occur with large cell abundances. Cell concentrations of 10^5 to 10^6 per ml are common in large blooms.

The Cairngorm Mountains in north east Scotland is the only sub-arctic site in the UK, providing a unique climate, ecology and terrain, with a mixture of continental and oceanic climates. The area receives over 100 days of snowfall per year and has the only perennial snow cover in the UK [9]. Ice/snow containing red snow algae (Fig. 1) located on Cairn Gorm in the Cairngorm Mountains was aseptically collected in July 2007. The sampling site was located 150 m north east from the summit of Cairn Gorm at an altitude of 1100 m above sea level. The site was in a sheltered aspect, protected from the prevailing wind, where snow from the previous winter had survived through until late summer. Samples of ice/snow containing the snow algae were transferred in a frozen state to the laboratory and stored at -10ºC. The samples have been analysed for biological markers with SERS (Surface–Enhanced Raman Spectroscopy) and GC-MS.

Fig. 2. Red snow algae on surface of snow/ice, Cairn Gorm, Scotland.

SERS data: A spectrum from a sample extract yields a SERS spectrum by adsorption onto silver-coated 1 micron diameter beads in a DMSO/water solution. The spectrum shows a number of peaks. Comparison with two pigment types, scytonemin and β,β carotene, shows a broad match with the Raman shift peaks for carotene (Fig. 3), indicating the presence of carotenoids.

Future Planetary Exploration: The Pasteur payload for the EXOMARS rover includes a LIBS-Raman instrument that can perform Raman Spectroscopy as both a first responder probe and in a microscopy format, but does not have a SERS capability. The next generation of Raman instruments deployed on the surface of Mars could possess a combination of Tele-Raman, Micro-Raman and LOC-SERS analysis capabilities and thus maximise the scientific return from mass dedicated to monochromatic light sources and Raman spectrometers.

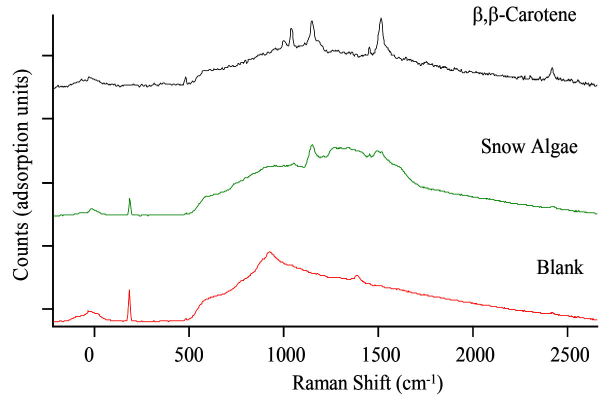

Fig. 3. Spectra obtained from sample containg red snow algae, Cairn Gorm, compared against β,β carotene standard, and laboratory blank. Integration time 4 secs; 532 nm source at 10 mW; Sample peaks match with carotene (Raman shift peaks around 1200 and just above 1500 cm^{-1}), indicating red pigments are carotenoids.

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