

**DETECTING REDUCED CARBON ON MARS USING RLS: RAMAN SPECTROSCOPY OF MARS ANALOGUES IN PREPARATION FOR EXOMARS.** L. V. Harris<sup>1\*</sup>, M. McHugh<sup>1</sup>, I. B. Hutchinson<sup>1</sup>, R. Ingle<sup>1</sup>, J. Parnell<sup>2</sup> and H. G. M. Edwards<sup>1</sup>, <sup>1</sup>Department of Physics and Astronomy, Space Research Centre, University of Leicester, University Road, Leicester LE1 7RH, UK, <sup>2</sup>Department of Geology and Petroleum Geology, University of Aberdeen, Aberdeen AB24 3UE, UK. (\*Correspondence email: liam.harris@leicester.ac.uk)

**Introduction:** The Raman Laser Spectrometer (RLS), one of the astrobiology instruments to be incorporated in the analytical laboratory of the ExoMars rover, currently due for launch in 2018, will likely be the first Raman instrument to be flown on a space mission. It is hoped that RLS will play a significant role in the completion of the mission's scientific objectives: to characterise the geochemical environment of the surface and subsurface (using the rover's 2 m long drill) and to search for biomarkers indicative of extant or extinct life [1].

One potential biomarker that is a high priority target for ExoMars is reduced carbon. Although reduced carbon has to date not been detected on Mars, they have been found in Martian meteorites [2]. If reduced carbon is discovered on Mars it could be the remnant of extinct microbial life, or alternatively it could act as a feedstock for extant life, in either case highlighting a potential habitat which deserves further investigation [3].

A number of carbon-rich Mars analogues have already been studied in order to demonstrate the detection and analysis of reduced carbon using flight-representative instrumentation [3][4]. The aim of this poster is to review that work in preparation for ExoMars and RLS and to present analysis of a new analogue sample which demonstrates how the environment can alter the Raman spectrum of carbon and how this affects its analysis.

**Methodology:** *Analogue sample:* Core samples of Devonian carbonaceous mudstone were taken from Caithness, Northern Scotland. In the image in **Fig. 1**, a layer of oxidised material can clearly be seen as a red band at the top of the sample. This kind of environmental alteration is expected to occur on Mars as a result of the planet's highly oxidising regolith, making this sample an ideal analogue.

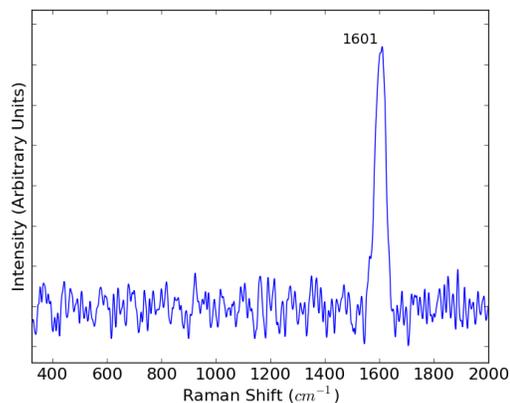
*Flight-representative instrumentation:* Raman spectra were acquired from the sample using instrumentation representative of RLS. The spectrometer used was equipped with a 100 mW, 532 nm laser with a footprint of <200  $\mu\text{m}$ . The instrument used a thermoelectrically cooled CCD detector and was capable of a maximum spectral resolution of 10  $\text{cm}^{-1}$  over its spectral range from 200 to 3400  $\text{cm}^{-1}$ .



**Fig. 1.** An image of a carbonaceous mudstone analogue from Caithness, Northern Scotland. The red colour of the top layer indicates the presence of haematite-rich, oxidised material.

Three regions of interest were visually identified on the sample: the red layer of oxidised material, the light grey unoxidised rock and the darker coloured sediment within that. Each of the three regions was randomly sampled, with Raman spectra acquired from several sites within each region to ensure homogeneity.

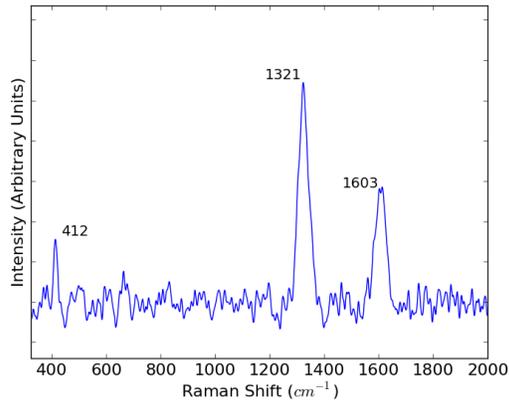
**Results and Discussion:** A representative Raman spectrum from the dark grey, unoxidised regions can be seen in **Fig. 2**. The only band visible, with a Raman shift of 1601  $\text{cm}^{-1}$ , is the  $\text{sp}^2$  band of the carbon spectrum. This indicates that the carbon present in this re-



**Fig. 2.** Raman spectrum of the dark grey, unoxidised mudstone.

gion of the rock consists almost entirely of  $sp^2$  carbons.

By comparison, spectra from the layer of red, oxidised material (**Fig. 3**) contain both the  $sp^3$  and  $sp^2$  carbon bands. Another Raman band with a shift of  $412\text{ cm}^{-1}$  is also visible in **Fig. 3**, likely the strongest band in the spectrum of the haematite that has been produced by oxidation.



**Fig. 3. Raman spectrum of the layer of red, unoxidised material.**

**Summary and Conclusion:** Reduced carbon has successfully been detected in a Mars analogue using a Raman spectrometer which is representative of the RLS instrument onboard the ExoMars rover. It has been determined that the oxidation process has transformed part of the rock, precipitating haematite and causing the dark red colour and that the Raman spectrum of the carbon has been altered. Since the positions and widths of the bands in the carbon spectrum can be used to distinguish between different populations of carbon, it will be important to understand this process before analysing spectra from RLS.

Future work will involve producing Raman spectra along a transect across the boundary between oxidised and unoxidised material. This will enable a more thorough analysis of the alteration to the carbon Raman spectrum.

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**References:** [1] Vago J. *et al.* (2013) *ESA Bull.*, 155, 12–23. [2] Steele A. *et al.* (2012) *Science*, 337(6091), 212–215. [3] Parnell J. *et al.* (2014) *Int. J. Astrobiol.* 13(2), 124–131. [4] Hutchinson I. B. *et al.* (2014) *Planet. Space Sci.* Manuscript submitted for publication.