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Detection of reduced carbon in basalt using Raman spectroscopy: a signpost to habitat on Mars

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1. Introduction

In the search for evidence of the environmental history of the Martian surface, and the possibility of life at some stage in the planet's history, a key component is reduced carbon. Carbon is available to the surface environment through meteoritic infall [1] and erosion of abundant volcanic rocks which contain magmatic carbon [2][3], in addition to the possibility of some biogenic carbonaceous matter. However, reduced carbon has not yet been detected by a range of missions to Mars. Carbonate minerals, containing carbon in inorganic oxidized form, have been recorded [4], which together with carbon dioxide in the Martian atmosphere and magmatic carbon in Martian meteorites provide evidence for a carbon cycle on Mars [5][6]. The mobility of carbon on Mars is also evident in fracture-bound carbon in the Nakhla meteorite, derived from Martian basalt [7] [8]. Basalts are widespread on Mars, so are readily accessible for sampling and analysis.

Basalt-hosted carbon could have a relationship to life in both a consequential or causative manner. Basalt could incorporate carbon from organic matter disseminated in sediments through which the basaltic magma passed. It is even possible that basalt could concentrate carbon scavenged from sediments into carbon-rich structures. Alternatively, basalt could act as a feedstock of carbon to provide biomass for colonizing microbes. In this way, the discovery of carbon in (Martian) basalt could be regarded as a signpost to habitat, i.e. the identification of carbon is a key aspect of the strategy for targeting where evidence of life should be sought.

The ExoMars mission, currently intended to fly in 2018, includes a Raman spectroscopy instrument, whose targets for detection include reduced carbon. We report here the study of an analogue for the carbon-bearing Nakhla meteorite, representing near-surface Martian crust, using Raman spectroscopy and other techniques to demonstrate the potential to detect the reduced carbon therein. The analogue is a terrestrial basalt containing traces of reduced carbon in cross-cutting fractures.

1.1 Geological setting

The analogue sample site is at Helen's Bay, County Down, Northern Ireland. Samples were taken from a coastal exposure of Upper Ordovician (Caradoc) pillow lava, formed on the floor of the Iapetus Ocean, described by [9] and [10]. The pillow lava is cross-cut by millimeter-scale veinlets of quartz with traces of carbon. The margins of the veinlets are red due to haematite precipitation, reflecting regional oxidative alteration during the Permo-Triassic [11].

2. Methodology and Results

Raman spectra of the sample, an example of which can be seen in Figure 1, were obtained using a portable Raman spectrometer. The spectrometer operates with an excitation wavelength of 532nm - the same as planned for the Raman instrument due to fly onboard the ExoMars rover.

A number of spectra were taken at different positions in three separate regions of interest on the surface of the rock. These were a carbon-containing quartz veinlet, a grey coloured homogeneous surface and a black surface embedded with crystalline structures. Quartz and carbon were identified in and around the veinlet, with both the D and G carbon bands visible in the spectra. The grey and black surfaces both gave Raman bands for carbon and anatase, although the signal-to-noise of spectra from the grey surface was poorer. Similar measurements were also obtained from crushed specimens of the rock (with a particle size distribution similar to that expected from the ExoMars Sample Prepartion and Distribution System). The Raman shift and FWHM of the carbon

G band was measured in each spectrum and represented on the cross-plot shown in Figure 2.

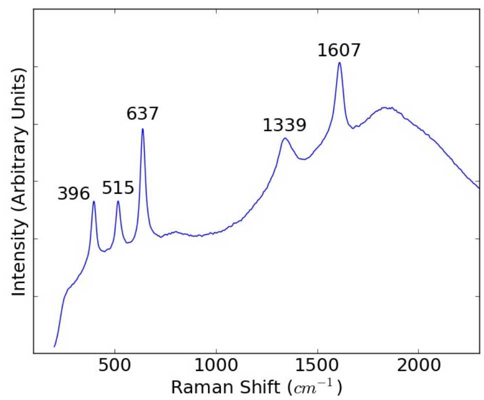

Figure 1: Typical Raman spectrum from the grey and black surfaces on the Helen's Bay sample.

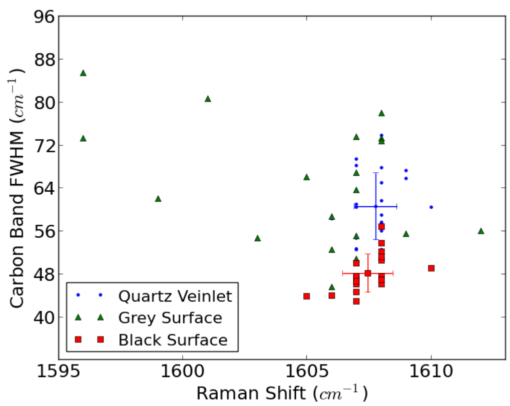

Figure 2: Cross-plot showing the Raman shift and FWHM of the carbon G band in three regions on the surface of the Helen's Bay sample. The points with error bars represent the mean position of each region.

Figure 2 shows that the carbon in the veinlet and that on the black surface of the rock represents two distinct populations (composition is less clearly defined for the grey areas). This demonstrates the use of Raman to distinguish between sources of carbon in a sample. Ongoing work suggests that the same is possible using crushed rock samples which is of relevance to the ExoMars mission and its method of sample delivery.

3. Summary and Conclusions

Reduced carbon has successfully been detected in a basaltic analogue of Mars by Raman spectroscopy. This was accomplished using an ExoMars flight-like spectrometer, with the same excitation wavelength and mode of operation. By comparing the Raman shift and FWHM of the carbon G band in spectra taken from different locations on the surface of the sample rock (and crushed specimens), at least two different populations of carbon can be identified.

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