PLANTARY EXPLORATION WITH A RAMAN SPECTROMETER: A STUDY OF CARBONACEOUS MATERIAL USING PORTABLE INSTRUMENTATION (532 & 785 NM). L. V. Harris\textsuperscript{1,*}, I. B. Hutchinson\textsuperscript{1}, R. Ingle\textsuperscript{1}, C. P. Marshall\textsuperscript{2}, A. Olcott Marshall\textsuperscript{2} and H. G. M. Edwards\textsuperscript{1}, \textsuperscript{1}Department of Physics and Astronomy, Space Research Centre, University of Leicester, University Road, Leicester LE1 7RH, UK, \textsuperscript{2}Department of Geology, University of Kansas, Lawrence, Kansas 66045, USA. (*Correspondence email: liam.harris@leicester.ac.uk)

Introduction: Raman spectroscopy has the potential to be an extremely powerful tool for remote robotic planetary exploration. Its ability to unambiguously identify both organic and inorganic molecules makes a Raman spectrometer well suited for use as both a geological and an astrobiological instrument [1]. Raman analysis also typically requires no mechanical or chemical sample preparation and is a nondestructive process, so would be an ideal first-pass method of analysis for a planetary exploration mission.

The first Raman instrument to be flown on a space mission is likely to be the Raman Laser Spectrometer (RLS) onboard the ExoMars rover [2]. The rover, the second element of the ExoMars mission [3], is due to launch in 2018. Once on Mars, its mission will be to: characterise the subsurface geochemistry (to a depth of 2 m), assess past and present habitability and search for signs of extinct or extant life (e.g. in the form of ancient deposits of carbonaceous material; CM).

The detection and analysis of CM is a primary goal of the ExoMars rover mission and will also be a focus of planetary exploration missions planned for the near future [4]. The presence of CM could be associated with either a remnant of living organisms or a potential feedstock, either way indicating a possible habitat and therefore a site to be investigated further by other instruments [5]. It has previously been demonstrated that Raman spectroscopy can be readily used to study various forms of carbon, including CM deposits in rock samples [6][7]. A good source of analogue samples (i.e. similar to those that might be investigated by a planetary rover on Mars) are Archaean cherts such as those found in the Pilbara Supergroup (e.g. [8]) that makes up part of the Pilbara Craton, Western Australia. Samples from this region have been characterised using a variety of Raman instruments in the past (e.g. [9]) and recent work has questioned which excitation wavelength is best suited for in-situ CM analysis [10].

The goals of this work were firstly, to demonstrate the acquisition of Raman spectra from samples of carbon-rich Archaean chert (some of the oldest known rocks on the planet) using a portable spectrometer with properties similar to those expected to be incorporated in future planetary missions and secondly, to compare the capabilities of a green (532 nm) and a red (785 nm) spectrometer in the analysis of CM.

Methodology: A total of 12 Archaean chert samples have been studied, each a member of the Pilbara Supergroup. Four of the samples (DFM1-4) were specimens of the ca. 3.49 Ga Dresser Formation chert-barite unit (the oldest samples in the set; e.g. [11]) and a further five (AC1-5) were examples of the ca. 3.46 Ga Apex Chert (e.g. [12]), both belonging to the Warrawoona Group (e.g. [13]). The remaining three samples (SPC1-3) were from the ca. 3.43 Ga Strelley Pool Chert (e.g. [14]), a member of the Kelly Group [15].

Raman spectra were acquired from each of the twelve samples using two flight-representative Raman spectrometers. The first was a DeltaNu Advantage 532 benchtop instrument (equipped with a 100 mW, 532 nm laser) capable of achieving a spectral resolution of <10 cm\(^{-1}\) over the 200 to 3400 cm\(^{-1}\) spectral range. The second was a DeltaNu Inspector 785 handheld spectrometer, which uses a 785 nm near-infrared laser with a maximum output power of 120 mW. The instrument covers a spectral range from 100 to 2000 cm\(^{-1}\) and has a spectral resolution of <8 cm\(^{-1}\).

A number of sites on the surface of each rock were investigated in order to assess sample homogeneity. Spectra were acquired in approximately 5 positions in a representative region in order to calculate mean band position, width and intensity and where possible, the same region was investigated using both instruments.

Results and Discussion: Silica (\(\text{SiO}_2\)) was found to be present in all twelve samples (as expected for a chert matrix), using both excitation wavelengths - in each case, clearly identified by the strong Raman band located at 465 cm\(^{-1}\) [16]. However, the lack of any corroborative bands means that it is not possible to directly determine which form this silica takes.

CM was readily detected in all of the samples with the 785 nm spectrometer and in half of the samples (AC5, DFM1-4, SPC2) with the 532 nm spectrometer - identified by the so-called disorder-induced and graphite (D and G) bands which typically exhibit Raman shifts of around 1350 and 1580-1600 cm\(^{-1}\) respectively [17]. As expected [18], the position of the D band is observed to be excitation wavelength dependent (i.e. it is dispersive) and in the spectra acquired with the 785 nm instrument, exhibits a D band Raman shift which is (on average) 38 cm\(^{-1}\) lower than in spectra acquired with an excitation wavelength of 532 nm (Fig. 1).

Aside from the dispersive D band, there are other considerable differences between the spectra acquired
with the different excitation wavelengths. This is illustrated (for DFM1) in Fig. 1 where it can be seen that the fluorescent background is much more intense in the 532 nm spectrum and that following background subtraction, the signal-to-noise ratio is poorer, making it more difficult to detect and analyse the CM using a 532 nm source. Additionally, no CM was detected in AC1-4 or SPC2-3 using 532 nm. The sample AC1 in particular was carefully examined in order to confirm this. Following the successful detection of CM using 785 nm, the same region of the rock’s surface was intensively searched using the 532 nm instrument. The instrument was operated in a wide range of modes but none were found that made a positive detection.

It has been demonstrated in previous work [19][20] that a comparison of the position and width of the G band in spectra from different samples can help to distinguish different types/sources of carbon. Fig. 2 shows a cross-plot of G band width against position for the spectra acquired in this study.

**Summary and Conclusion:** Raman spectra have been acquired for twelve samples of ca. 3.42-3.49 Ga Archaean chert from the Pilbara Craton, Western Australia, using portable (flight-like) spectrometers, with laser excitation wavelengths of 532 and 785 nm.

Every sample was found to contain silica (SiO$_2$) and deposits of carbonaceous material (identified by the presence of both carbon D and G bands). The carbon spectra were more readily acquired with an excitation wavelength of 785 nm. Additionally in those samples where spectra were acquired at both wavelengths, the fluorescent background was more intense and the signal-to-noise ratio reduced in the 532 nm spectra. All science requirements of an instrument must be considered when selecting excitation wavelength however, for example the 532 nm laser used by RLS is more suitable for detecting and characterising biological pigments. This work has demonstrated that it will be possible to detect and characterise CM on Mars using RLS, but that there are advantages to using 785 nm for some sample types if CM analysis is the primary goal.

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**References:**