Selection of Portable Spectrometers for Planetary Exploration: A Comparison of 532 nm and 785 nm Raman Spectroscopy of Reduced Carbon in Archean Cherts

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Abstract

Knowledge and understanding of the martian environment has advanced greatly over the past two decades, beginning with NASA's return to the surface of Mars with the Pathfinder mission and its rover Sojourner in 1997 and continuing today with data being returned by the Curiosity rover. Reduced carbon, however, is yet to be detected on the martian surface, despite its abundance in meteorites originating from the planet. If carbon is detected on Mars, it could be a remnant of extinct life, although an abiotic source is much more likely. If the latter is the case, environmental carbonaceous material would still provide a source of carbon that could be utilized by microbial life for biochemical synthesis and could therefore act as a marker for potential habitats, indicating regions that should be investigated further. For this reason, the detection and characterization of reduced or organic carbon is a top priority for both the ESA/Roscosmos ExoMars rover, currently due for launch in 2018, and for NASA's Mars 2020 mission. Here, we present a Raman spectroscopic study of Archean chert Mars analog samples from the Pilbara Craton, Western Australia. Raman spectra were acquired with a flight-representative 532 nm instrument and a 785 nm instrument with similar operating parameters. Reduced carbon was successfully detected with both instruments; however, its Raman bands were detected more readily with 785 nm excitation, and the corresponding spectra exhibited superior signal-to-noise ratios and reduced background levels. Key Words: Raman spectroscopy—Archean—Organic matter—Planetary science—Mars. *Astrobiology* 15, 420–429.

1. Introduction

THE SEARCH FOR SIGNS of extant and extinct life is one of the primary objectives of current Mars exploration missions (Mustard *et al.*, 2013; Vago *et al.*, 2013) and a number of future missions to other bodies in the Solar System, such as the icy jovian moon Europa (Pappalardo *et al.*, 2013) or Titan, Saturn's liquid hydrocarbon-covered moon (Lorenz *et al.*, 2005).

The detection and characterization of ancient carbonaceous material (CM) will play an important role in this search, as any reduced carbon (crystalline sp^2 hybridized CM) in an environment could be a remnant of living organisms, or at the very least could provide a source of carbon for incorporation into biochemical molecules and

structures by microbial life (Petsch *et al.*, 2001; Parnell *et al.*, 2014). Either way, the presence of reduced carbon would indicate a potential habitat that should be studied more closely (Harris *et al.*, 2013). Reduced carbon, in the context of this paper, is defined as macromolecular carbon that is a product of the geological processing of organic debris (hydrocarbons of either biotic or abiotic origin). Such processing results in the graphitization of deposited hydrocarbons, which strips them of hydrogen atoms and functional groups and produces increasingly large and complex aromatic carbon units (more ordered carbon) with perfect graphite as the end-point (Buseck and Huang, 1985). Reduced carbon describes material from any stage in this process, in the transition from amorphous carbon to graphite, and so includes carbon of a range of thermal maturities

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and therefore levels of order. Reduced or incompletely crystallized carbon goes by a number of other names in the literature, including amorphous carbon, disordered carbon, and nanocrystalline graphite (Ferrari and Robertson, 2000).

Raman spectroscopy has been used with great success in the laboratory analysis of carbon for decades (for a comprehensive review, see the work of Saito *et al.*, 2011, and references therein) and more recently for the detection of CM in a variety of mineral matrices (*e.g.*, Marshall *et al.*, 2010; Olcott Marshall *et al.*, 2012; Hutchinson *et al.*, 2014). Flight designs for Raman spectrometers are at a mature stage (Wang *et al.*, 2003; Lopez-Reyes *et al.*, 2013), and the Raman Laser Spectrometer (RLS) on board the ExoMars rover, which is due to be launched in 2018, will be the first Raman instrument to be flown on a space mission. Reduced carbon will be one of the highest-priority targets (Edwards *et al.*, 2014).

ExoMars is a planetary exploration and astrobiology program consisting of two separate missions, operated jointly by the European Space Agency (ESA) and the Russian Federal Space Agency (Roscosmos) as part of ESA's Aurora program. The first mission will incorporate the Trace Gas Orbiter (TGO) and the Entry, Descent and Landing Demonstrator Module (EDM) and is currently due for launch in January 2016. Once in orbit, the TGO will investigate trace gases in the tenuous martian atmosphere (using two spectroscopic instruments covering a broad wavelength range; Vandaele *et al.*, 2011; Trokhimovskiy *et al.*, 2014), attempt to identify their source, and establish their biogenicity. Meanwhile, the EDM will be used to demonstrate ESA and Roscosmos' ability to successfully deliver a payload to the surface of the planet. The second mission will be the ExoMars rover, which is currently scheduled for launch in May, 2018. The science aims of the rover mission are to characterize the geochemistry and water environment of the martian surface and subsurface (down to a depth of 2 m) and search for signs of extant or extinct life. It will achieve this by extracting rock core samples with a 2 m long drill, crushing them, and analyzing the crushed material with its onboard suite of analytical instruments, which will include the RLS (Rull *et al.*, 2011; Edwards *et al.*, 2012; Vago *et al.*, 2013).

1.1. Raman spectroscopy

Raman spectroscopy is a molecular analysis technique that is based on the phenomenon of Raman scattering (Raman and Krishnan, 1928). It can be used to probe the bond structure of molecules and thereby provide molecular identification (Smith and Dent, 2004). It is a well-established technique in many fields for a wide variety of applications, including pharmaceutical analysis, pigment identification in archaeological dating (and validation), and the detection of narcotics and explosive materials. Further, the potential of Raman spectroscopy as a powerful tool for remote robotic planetary exploration has been recognized with its inclusion in the ExoMars rover's analytical laboratory and the straw-man payloads of a number of future missions (*e.g.*, Mustard *et al.*, 2013). The technique has a number of advantages that make it particularly well suited for both geological and astrobiological studies (Jorge Villar and Edwards, 2006). Raman spectroscopy can unambiguously identify both organic and inorganic molecules, and its

acquisition times are short (from a few seconds to a few minutes). Raman spectroscopy also typically requires no mechanical or chemical sample preparation and is a non-destructive process, which makes it an ideal first-pass analysis method for a planetary exploration mission.

One limitation of Raman spectroscopy as an analytical technique is the simultaneous fluorescence of an illuminated sample. If incident light is able to excite an electronic transition in molecules in a target, upon relaxation they will re-emit, usually in the visible region of the spectrum, producing a broad, smooth continuum upon which the spectrum will be superimposed. Depending on the intensity of the Raman signal, such a fluorescent background and the associated noise (both Poissonian and that incurred by background subtraction processing) may be prohibitive in the detection of Raman bands and thus hinder molecular identification. There are a number of possible methods of reducing the influence of fluorescence, including intelligent selection of the excitation source wavelength (Jorge Villar *et al.*, 2005). When using a visible source such as the 532 nm laser to be used by the RLS, fluorescence will be a problem; however, the resonance effect that occurs in organic molecules at this wavelength means they are readily detected. Upon shifting to a UV excitation source (*e.g.*, 248 nm), the fluorescence becomes spectrally separated from the Raman signal since it occurs at a fixed wavelength, whereas Raman shifts are relative to the excitation wavelength (Kohel *et al.*, 2010). This produces spectra with an almost flat baseline. There are some challenges with UV Raman, however, such as the increased risk of chemical alteration of samples due to the increase in photon energy. The energy of a 248.6 nm photon is ~ 5 eV, which is greater than typical binding energies of atoms in an organic molecule and thus enables a laser of this wavelength to degrade organics quite readily, even without thermal damage. Further challenges with UV Raman include the additional cost of UV optics and detectors and the low space technology readiness level of the necessary components. Alternatively, an IR excitation source could be used (*e.g.*, 785 or 1064 nm) whose photons would have insufficient energy to induce electronic excitation in most molecules and thus prohibit fluorescence. Due to the proportionality between Raman intensity and λ^{-4} , however, this would also cause a reduction in the Raman signal, which for certain samples could result in insufficient signal-to-noise ratios (Vítek *et al.*, 2012a).

Although excitation wavelength selection for flight instrumentation has been discussed extensively in the literature (Vítek *et al.*, 2012b; Wang, 2012), only spectrometers that use green (Rull *et al.*, 2011; Clegg *et al.*, 2014) and UV (Beegle *et al.*, 2014) excitation have been successfully proposed for space missions to date. Near-infrared (NIR) Raman spectroscopy is usually considered most suitable for the study of ancient materials such as reduced carbon deposits, so in light of the current interest in detecting such materials on Mars, it is important to evaluate the performance of portable NIR Raman spectrometers. As such, the aims of this work were to investigate the use of portable Raman spectrometers to acquire reduced carbon spectra from Mars analogues, comparing the results of using 532 and 785 nm excitation sources, and to offer recommendations on the design of instruments for planetary exploration.

2. Materials and Methods

2.1. Geological setting

A good source of analog samples that contain CM, which are representative of those that might be investigated by a planetary rover on Mars, are Archean cherts such as those found in the Pilbara Supergroup (*e.g.*, Van Kranendonk, 2006) that are contained within the Pilbara Craton, Western Australia. The 3.53–3.17 Ga East Pilbara Terrane, in the northeast of the Pilbara Craton, contains both the 3.525 Ga to 3.427 Ga Warrawoona Group and the younger Kelly Group (Van Kranendonk *et al.*, 2007). Although the Warrawoona Group primarily represents volcanic deposition, the *ca.* 3.49 Ga chert-barite Dresser Formation, in the lower part of the Group, shows signs of subaerial deposition (Van Kranendonk and Pirajno, 2004; Van Kranendonk *et al.*, 2007, 2008). The Apex Basalt, found in the upper Warrawoona Group, contains a stratiform chert layer pierced by synsedimentary hydrothermal fracture-fill veins informally referred to as the Apex chert (Brasier *et al.*, 2011). The Kelly Group overlies the Warrawoona Group unconformably, across an erosional surface; the oldest unit in the Kelly Group is the *ca.* 3.43 Ga sedimentary Strelley Pool Chert (Van Kranendonk, 2006; Van Kranendonk *et al.*, 2007). In this work, a total of 12 samples of chert from the East Pilbara Terrane were studied: four (referred to as DFM1–DFM4) from the Dresser Formation; five (referred to as AC1–AC5) from the *ca.* 3.46 Ga Apex chert (*e.g.*, Marshall *et al.*, 2011; Olcott Marshall *et al.*, 2012, 2014); and the remaining three (referred to as SPC1–SPC3) from Strelley Pool chert (*e.g.*, Allwood *et al.*, 2006).

2.2. Instrumentation

Raman spectra were acquired from the 12 chert samples described in Section 2.1 with two different commercial Raman spectrometers, each with flight-representative operating modes and parameters. The first was a DeltaNu Advantage 532 benchtop instrument with a mass of 5–6 kg, which uses a 100 mW, 532 nm continuous wave (CW) laser and is capable of achieving a spectral resolution of $<10\text{ cm}^{-1}$ over its 200–3400 cm^{-1} spectral range, with an irradiance at the sample of $\sim 1.6\text{ kW}\cdot\text{cm}^{-2}$ in a $50\text{ }\mu\text{m}$ spot (all comparable parameters to those proposed for the RLS). The second instrument was a DeltaNu Inspector 785 handheld spectrometer, which uses a 785 nm CW NIR laser with a maximum output power of 120 mW. This instrument covers a spectral range from 100 to 2000 cm^{-1} and has a spectral resolution of $<8\text{ cm}^{-1}$. The irradiance at the sample is $\sim 0.7\text{ kW}\cdot\text{cm}^{-2}$ in a $75\text{ }\mu\text{m}$ spot. Spectra were acquired without the use of a microscope image. For comparison, the RLS flight instrument will use a 531.5 nm CW laser, focused onto a $50\pm 10\text{ }\mu\text{m}$ spot at the sample with an irradiance of $0.6\text{--}1.2\text{ kW}\cdot\text{cm}^{-2}$. The spectral resolution will be $\leq 6\text{ cm}^{-1}$ below 2000 cm^{-1} and $\leq 8\text{ cm}^{-1}$ above 2000 cm^{-1} , across a spectral range of 200–3800 cm^{-1} .

2.3. Spectral acquisition

Initially, the 12 samples were visually examined to identify specific regions of interest (areas on the surface of different colors and textures and with obvious crystals or other macroscopic features). Several Raman spectra were

acquired from each region to determine their typical spectra and enable averaging of spectral parameters. Laser power and spectral integration time were optimized to make full use of the dynamic range of the detector while avoiding thermal alteration of the samples.

3. Results

The spectra acquired from all 12 chert samples exhibit a strong, narrow Raman band with an average Raman shift of $466\pm 2\text{ cm}^{-1}$ (Fig. 1). This band results from the movement of the oxygen atom in a Si-O-Si totally symmetric stretching mode and was assigned a relative wavenumber of 465 cm^{-1} by Kingma and Hemley (1994). The band indicates the presence of crystalline silica (SiO_2). The detection of the weaker corroborative bands expected in the 200–400 cm^{-1} region was limited by the background signal and effects of the laser excitation cutoff filter.

Figure 2 shows the Raman spectrum of a green region on the surface of sample AC1, with bands at shifts of 1005, 1157, and 1519 cm^{-1} , corresponding to the spectrum of a carotenoid molecule (de Oliveira *et al.*, 2010). This is clearly a modern microbial colonization, as evidenced by the bright green color of the rock surface; however, it is still of interest to compare the ability of the portable spectrometers to detect biomarkers such as carotenoids. It was only possible to acquire this spectrum with the 532 nm instrument, which is attributed to the fact that there is a resonance enhancement of the carotenoid spectrum with the excitation wavelength (Marshall *et al.*, 2007a; Viték *et al.*, 2009a).

Hematite [iron(III) oxide; $\alpha\text{-Fe}_2\text{O}_3$] was also detected in a number of the chert samples, particularly SPC3 (Fig. 3), which is identifiable by bands with Raman shifts of 294, 409, 496, and 611 cm^{-1} . In addition to these bands, two broad bands can be observed in the spectrum of hematite at *ca.* 660 and 1320 cm^{-1} . The band at *ca.* 660 cm^{-1} has been assigned to an odd symmetry IR-active phonon mode, which is allowed to become active due to lattice defects and decreasing crystallite size (Shim and Duffy, 2002). The odd

FIG. 1. A Raman spectrum of silica, acquired from the sample AC1 by using 532 nm excitation with an integration time of 50 s. The fluorescence background has been reduced with Fourier transform background subtraction.

FIG. 2. Left: An image of the sample AC1, with a green-colored region of interest on the surface marked with an arrow. Right: Raman spectrum from the green region, acquired by using a 532 nm excitation source with a 30 s integration time. The Raman bands at 1005, 1157, and 1519 cm^{-1} are indicative of a carotenoid. The fluorescence background has been reduced with Fourier transform background subtraction. Color images available online at www.liebertonline.com/ast

symmetry IR-active phonon mode is not observed in our spectra. However, the strong intensity broad band at $\text{ca. } 1320 \text{ cm}^{-1}$ that is attributed to an overtone band of the $\text{ca. } 660 \text{ cm}^{-1}$ first-order mode is present in our spectra. The overtone band at $\text{ca. } 1320 \text{ cm}^{-1}$ is much stronger in intensity than the first-order band at $\text{ca. } 660 \text{ cm}^{-1}$, which is often absent in most spectra due to its low intensity. Hematite was only readily detectable when using the 785 nm instrument, as 532 nm light is largely absorbed by the often red-colored hematite.

3.1. Reduced carbon analysis

In addition to the ubiquitous silica matrix and other molecules described above, Raman spectra from certain

FIG. 3. A hematite spectrum from the sample SPC3, acquired with a 785 nm instrument and an integration time of 60 s. The background signal has been reduced with Fourier transform background subtraction.

regions of some of the chert samples also reveal the presence of reduced carbon (Fig. 4), which is identifiable by the so-called *D* and *G* bands in its spectrum, with Raman shifts of 1350 cm^{-1} and between 1580 and 1600 cm^{-1} , respectively (Ferrari and Robertson, 2000). The *D* band occurs as a result of a breathing mode of sp^2 hybridized carbon atoms in six-fold aromatic rings that becomes Raman active with disorder and decreasing crystallinity and is forbidden in pure graphite or graphene, as well as in completely amorphous carbon (a-C), whereas the *G* band results from the in-plane stretching mode of any two or more sp^2 carbon atoms (Ferrari and Robertson, 2000). This means that the CM deposited in the chert samples, with both bands in its spectrum, is made up of disordered sp^2 nanocrystalline graphite.

As reported previously by a number of other groups (Wang *et al.*, 1990; Matthews *et al.*, 1999), the position of the carbon *D* band is seen to be dependent on the wavelength of the excitation source (*i.e.*, the band is dispersive). This dispersion was observed between spectra produced with 532 and 785 nm excitation in every chert sample for which spectra could be acquired with both instruments, with an average difference in the position of the *D* band of $38 \pm 4 \text{ cm}^{-1}$. Figure 5 shows a comparison of the spectra acquired from the same region of the surface of DFM1, in which the dispersive nature of the carbon *D* band is clearly demonstrated.

Carbonaceous material was detected much more readily with the 785 nm instrument than it was with the 532 nm instrument (*i.e.*, it was observed in all the samples with 785 nm excitation compared to only half the samples with 532 nm; see Table 1 for further details). In cases where carbon spectra could be acquired for a given sample with both instruments (*e.g.*, Fig. 5), those produced with 532 nm excitation exhibit a considerably more intense background (which is a consequence of fluorescence). The signal-to-noise ratio (SNR) of the two carbon bands is also reduced in the 532 nm spectra. Taking the noise to be the root mean square of the deviation from a polynomial fit to the

FIG. 4. An example Raman spectrum for the sample DFM1, acquired by using 532 nm excitation and a 60 s integration. The band at 465 cm^{-1} is from the spectrum of silica, while the bands at 1349 and 1603 cm^{-1} , respectively, are the *D* and *G* bands in the spectrum of reduced carbon.

background from 600 to 1200 cm^{-1} , the *D* and *G* bands have SNRs of only 11 and 12, respectively, on the 532 nm spectra, compared with 36 and 30 on the 785 nm.

In previous work (Parnell *et al.*, 2014), it has been demonstrated that comparison of the position and width of the carbon *G* band in different spectra can enable the differentiation of distinct sources of reduced carbon, assuming they possess different levels of structural disorder and therefore have different thermal histories. The centroid position and full width at half maximum (FWHM) of both the *D* and *G* bands were measured in the chert spectra. Figure 6 shows a cross-plot of *G* band width against position for the chert spectra acquired with both the 532 and 785 nm instruments, along with data points from a similar 532 nm study of a set of natural shale analogues for comparison. It was observed that measurement of these parameters on uncorrected spectra added a small systematic offset in the position to higher wavenumbers (of the order of a few wavenumbers) and a small increase in the uncertainty in measuring both parameters. To provide consistency, a linear fit to the background in a narrow window around the *G* band was subtracted prior to the measurement of its centroid position and FWHM. Fourier baseline correction of entire spectra was only used for the elucidation of bands and their presentation here.

FIG. 5. Stacked Raman spectra for DFM1, obtained with 532 nm (green) and 785 nm (red) lasers. Spectra were acquired by using a 60 s integration. Inset: Same spectra following Fourier transform background subtraction, in order to demonstrate that the band intensity variation is due to instrument differences and not the variation in the background. Color images available online at www.liebertonline.com/ast

TABLE 1. AN INDICATION OF THE SAMPLES IN WHICH CARBONACEOUS MATERIAL WAS POSITIVELY IDENTIFIED BY RAMAN SPECTROSCOPY AND THE EXCITATION WAVELENGTH WITH WHICH THIS WAS ACHIEVED

	532 nm	785 nm
DFM1	✓	✓
DFM2	✓	✓
DFM3	✓	✓
DFM4	✓	✓
AC1		✓
AC2		✓
AC3		✓
AC4		✓
AC5	✓	✓
SPC1		✓
SPC2	✓	✓
SPC3		✓

4. Discussion

There is a great deal of work in the literature detailing the detection of carotenoids (*e.g.*, Edwards *et al.*, 2005a; Vitek *et al.*, 2009b) and other biological pigment molecules such as scytonemin (*e.g.*, Edwards *et al.*, 2005b). Such pigments

are synthesized by a vast range of living organisms, including extremophiles that produce them as part of suites of protectant molecules to aid in the survival of such organisms in hostile environments (Sinha and Häder, 2008). These molecules have been used for some time as biomarkers in terrestrial environments (Jehlička *et al.*, 2014), and it has been suggested that they may also be suitable targets for planetary astrobiology missions (Parnell *et al.*, 2007; McKay *et al.*, 2008; Edwards, 2010; Edwards *et al.*, 2014).

Recent studies have indicated that the martian surface radiation environment will likely cause the degradation of carotenoids and similar biomolecules, altering the Raman spectra of any such biosignatures that may be present on Mars (Dartnell *et al.*, 2012). Ancient deposits of reduced carbon, however, are less likely to be affected by solar UV radiation and cosmic rays, providing a potentially more robust marker of habitat and biological activity. Reduced carbon could be a product of the thermal evolution of organic matter deposited within rock by generations of living organisms, making it a possible candidate biomarker for extinct life. Of course, any CM in an environment could have an abiotic source; however, it could still act as a source of carbon to be utilized by microbes, marking a potential habitat. It is not possible to determine the biogenicity of geological carbon with Raman spectroscopy (Pasteris and

FIG. 6. A cross plot of carbon G band width versus position by using 785 nm (filled circles) and 532 nm (open circles) excitation sources. Points marked with triangles, squares, and diamonds are from a similar study of natural shale samples (Hutchinson *et al.*, 2014). Error bars represent the standard deviation across many separate points on each sample, to include the uncertainty in both measurement of the band width and position as well as that associated with variations in the sample, such as crystal orientation, variations in absorbance, and sampling of the host matrix. Color images available online at www.liebertonline.com/ast

Wopenka, 2002, 2003; Marshall *et al.*, 2010); however, in the case of a planetary mission, a positive detection would indicate samples that should either be investigated further by using additional techniques capable of assessing biogenicity, or cached for future return to Earth for more detailed analysis (Mustard *et al.*, 2013).

The results presented here demonstrate the successful detection of reduced carbon in Archean cherts (selected as Mars analog samples) by using flight-representative Raman instrumentation. This has previously been accomplished *in situ* with the same portable 785 nm spectrometer (Olcott Marshall and Marshall, 2013), so here we extend that work by investigating 12 samples and comparing the results from that instrument and the 532 nm, benchtop spectrometer. This result is significant to both the ExoMars mission and any future planetary exploration missions that may include Raman spectrometers in their payload (Wang *et al.*, 2003; Lopez-Reyes *et al.*, 2013; Beegle *et al.*, 2014; Clegg *et al.*, 2014). The improvement in SNR and the reduction of the background (seen in Fig. 5) observed when acquiring spectra with the 785 nm instrument suggest that this may be the more appropriate wavelength to choose if the sole aim of the instrument is to detect and characterize CM of this type. Additionally, it was not possible to detect reduced carbon in six of the 12 samples investigated with the 532 nm instrument (Table 1). This suggests that carbon is more readily detected with 785 nm excitation, further supporting the selection of this wavelength for this kind of analysis. A space mission is usually given several scientific objectives, however, and therefore an included Raman instrument would likely have a number of high-priority targets. As a result, trade-offs must be made during the instrument development process, considering all mission objectives.

Once a CM spectrum has been acquired, measurement of certain spectral parameters can yield information on its exact structure and therefore indicate its level of thermal maturity. It has been demonstrated in the literature that the intensity ratios I_D/I_G and $I_D/(I_D + I_G)$ (where I_D and I_G are the intensities of the *D* and *G* bands, respectively) are inversely proportional to the crystallite diameter, L_a . The parameters also correlate with the level of structural disorder in a CM sample (Beny-Bassez and Rouzaud, 1985; Cuesta *et al.*, 1994) and with other metrics of disorder obtained from other analytical techniques, such as the H/C atomic ratio and the molecular MeP/P (summed methylphenanthrenes/phenanthrene) parameter (Marshall *et al.*, 2007b). For a lander or rover mission, however, it will be necessary to rely on parameters that are relatively simple to compute, due to the limitations of the instrument processor. It has been shown that, in some cases, information on the thermal maturity of a sample of CM can be gained simply by measuring the width and position of the carbon *G* band (Hutchinson *et al.*, 2014; Parnell *et al.*, 2014; this work). Figure 6 shows the results of these measurements for the cherts and a past study of natural shale samples for comparison and as a calibration of thermal maturity (Hutchinson *et al.*, 2014). This study demonstrated that it is possible to differentiate between shale samples of low, medium, and high thermal maturity by comparing carbon *G* and position and width, with thermal maturity tending to increase with increasing *G* band Raman shift and decreasing *G* band width. The

clustering of the data points from the Archean cherts precludes differentiation of samples of different thermal maturity within the sample set but does indicate that they are generally all of high maturity, which is expected for samples of this geological age and metamorphic grade (greenschist facies).

The scientific objectives of a mission are often broad and varied, however, so other considerations must be made when designing a flight instrument and its operating modes. In this study, it was possible to detect carotenoids in the sample AC1 with the green laser, due to a resonance enhancement effect—an example of how competing-priority targets often have different instrument requirements. This problem may be solved on future missions by including more than one Raman instrument in the payload (perhaps one incorporated in an analytical laboratory and another mounted on an arm) or by designing instruments with more than one excitation source (for which the mass penalty could be relatively small).

5. Conclusions and Implications

Reduced carbon was successfully detected in samples of Archean chert with a 532 nm Raman instrument with operating parameters and modes representative of the RLS, an instrument that will be incorporated in the analytical laboratory of the ExoMars rover. Carbon was also detected with a similar 785 nm instrument that was used to provide a performance comparison. For these particular samples, 785 nm appears to be the more suitable excitation wavelength for detecting and characterizing reduced carbon, as lower levels of fluorescence are encountered and improved SNRs can be attained (the carbon *D* and *G* bands had SNRs of 11 and 12, respectively, in the 532 nm spectra, whereas these were as high as 36 and 30 in the 785 nm). Furthermore, reduced carbon is more readily detected when using 785 nm excitation, having been detected in all 12 chert samples studied here, compared with 532 nm, which only made positive detections in half the samples. This could be due to the decrease in SNR and because bands are swamped by the background, or it could be due to differences in laser footprint size and penetration depth between the two instruments.

It is likely that reduced carbon would be one of only a small number of materials of potentially biological origin robust enough to persist on the surface of Mars, so the detection and characterization of ancient material such as reduced carbon is likely to be one of the primary scientific objectives of future missions of exploration. In this case, the recommendation would be to include a Raman instrument with a 785 nm excitation source in the payload. All currently proposed flight instruments utilize either green or UV excitation; however, laboratory studies over the past decade have shown that NIR Raman spectrometers are best suited to the analysis of ancient material. Furthermore, it has been demonstrated in this study that a NIR portable instrument, with comparable operating parameters to current flight designs, can readily detect both reduced carbon and host matrix minerals such as silica and hematite. Future proposals for Raman flight instruments should consider NIR excitation (at least to complement other excitation wavelengths).

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Author Disclosure Statement

All authors state that no competing financial interests exist.

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Abbreviations Used

CM = carbonaceous material
CW = continuous wave
EDM = Entry, Descent and Landing
Demonstrator Module
FWHM = full width at half maximum
NIR = near-infrared
RLS = Raman Laser Spectrometer
SNR = signal-to-noise ratio
TGO = Trace Gas Orbiter