**DEEP UV RAMAN SPECTROSCOPY OF ORGANIC CARBON: IMPLICATIONS FOR SHERLOC OBSERVATIONS ON MARS.** A. E. Murphy[1], S. Sharma[2], J. Razzell Hollis[3], A. Steele[4], R. Bhartia[5], R. S. Jakubek[6], M. D. Fries[7], W. J. Abbey[2], L. W. Beegle[8], R. A. Yingst[1]. [1]Planetary Science Institute, 1700 E. Ft. Lowell, Suite 106, Tucson, AZ 85719 (amurphy@psi.edu), [2]NASA Jet Propulsion Laboratory, Pasadena, CA 91109, [3]The Natural History Museum, London, UK, [4]Carnegie Institution for Science, Washington, DC 20015, [5]Photon Systems Incorporated, Covina, CA 91722, [6]Jacobs JETS, NASA Johnson Space Center, Houston, TX 77058, [7]NASA Johnson Space Center, Houston, TX 77058, [8]Formerly with NASA Jet Propulsion Laboratory, Pasadena, CA 91109.

**Introduction:** Mounted on the *Perseverance* rover's arm is SHERLOC (Scanning Habitable Environments with Raman & Luminescence for Organics & Chemicals), a deep ultraviolet (DUV, 248.6 nm excitation) Raman and fluorescence spectrometer that is optimized to detect organic molecules and can map areas up to 7 x 7 mm, allowing for the observation of important spatial relationships between organics and minerals [1,2]. DUV Raman is useful for detecting organic molecules due to its limited fluorescence interference, which at longer wavelengths (visible light or VIS) may obscure the Raman signal [3]. Although DUV Raman spectra of minerals and organic carbon have been reported [4-8], a thorough characterization of organic carbon using DUV and VIS (532 nm excitation) in ancient microbial-mediated carbonate rock and the investigation of deriving temperature information from DUV Raman D and G peak parameters, has not yet been reported.

Raman spectra of macromolecular carbon (D and G bands at ~1350 and 1600 $cm^{-1}$, respectively) may exhibit different peak parameters based on the excitation laser wavelength used [9]. Literature has focused on D and G band observations using 532 nm laser excitation, and the resulting peak parameters, such as the intensity ratio between D and G bands and full-width at half maximum (FWHM) of bands, have been used to establish geothermometry methods [10,11]. However, DUV Raman of D and G bands often display decreased D band intensity and increased G band intensity [12]. This difference in spectral response between DUV and VIS is important to understand when searching for organic carbon on Mars with SHERLOC, where the presence of a G band in relatively low signal-to-noise ratios (SNR) may not be easily identified. As *Perseverance* approaches the marginal carbonate unit [13] along the western crater rim of Jezero, it is pertinent that we compare what we know from VIS Raman studies of organic matter in carbonate rock to DUV Raman.

In this study, we analyze stromatolitic carbonate rocks [$CaMg(CO_3)_2$] using DUV Raman spectroscopy to detect and characterize organic carbon. D and G bands in DUV and VIS will be compared to answer the following questions: 1) How do D and G band parameters vary between DUV and VIS, 2) How might laser power and pulses per point (ppp) affect the Raman signal, and 3) Can VIS (532 nm) geothermometry be extrapolated to DUV.

**Materials and Methods:** Carbonate rock samples used in this study were previously characterized with 532 nm Raman spectroscopy [14].

Samples were analyzed on the SHERLOC analog instruments, MOBIUS (Mineralogy and Organic Based Investigations with UV Spectroscopy) and "Arthur" (flight analog brassboard), two custom DUV resonance Raman spectrometers at NASA Jet Propulsion Laboratory that utilize 248.6 nm NeCu pulsed lasers. MOBIUS acquisition settings were 1200 ppp, and for Arthur, a sequence of 5/25/100/400/800 ppp was used.

Raman D and G bands were fit with a Gaussian-Lorentz Area function using PeakFit 4.12 software. VIS Raman D and G bands were deconvolved into five peaks (D1, D2, D3, D4, and G) according to geothermometry methods [15]. Fitted VIS and DUV Raman D and G band positions and FWHM of the original and deconvolved spectra were recorded for comparison.

**Preliminary Results:** MOBIUS (DUV) results show only a G band in DUV, while VIS shows an approximate 1:1 intensity ratio between D and G bands (Fig. 1).

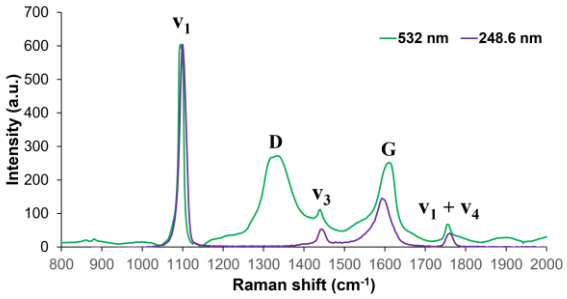


***Fig. 1*** *Overlay of characteristic visible (532 nm) and deep ultraviolet (248.6 nm) Raman spectra of stromatolite sample. Spectra intensity is normalized to the $v_1$ carbonate band. Organic carbon D and G bands and carbonate bands $v_3$ and $v_1$+$v_4$ are marked for reference. VIS and DUV Raman spectra shown here were collected at Carnegie by A. Steele and NASA JPL by S. Sharma, respectively.*

Results from the flight analog brassboard instrument (Arthur) show D and G bands with lower SNR,

similar to SHERLOC spectra collected on Mars, and the effect of increasing ppp on Raman signal will be studied using this data set.

Preliminary comparisons between VIS and DUV Raman spectra of D and G bands indicate VIS geothermometry methods may not be suitable for determining thermal maturity in DUV collected spectra. We will investigate the usefulness of a DUV Raman geothermometer by analyzing standards, with known formation (or alteration) temperatures, in VIS and DUV and comparing the results.

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**References:** [1] Abbey W. J. et al. (2017) *Icarus, 290*, 201-214. [2] Bhartia R. et al. (2021) *Space Sci. Rev., 217*, 58. [3] Asher S. (1993) *Anal. Chem., 65*, 201A-210A. [4] Razzel Hollis J. et al. (2022) *Planet. Spac. Sci., 209*, 105356. [5] Shkolyar S. et al. (2018) *Astrobiology, 18*, 431-453. [6] Osterhout J. et al. (2022) *Astrobiology, 22*, 1239-1254. [7] Czaja A. D. et al. (2009) *Org. Geochem., 40*, 353-364. [8] Ferrari A. C. and Robertson J. (2000) *Phys. Rev. B, 61*, 14095. [9] Merlen A. et al. (2017) *Coatings 7*, 153. [10] Wopenka B. and Pasteris J. D. (1993) *Am. Min., 78*, 533-557. [11] Beyssac, O. et al. (2002) *J. Metamorph. Geol., 20*, 859-871. [12] Ferrari A. C. et al. (2001) *Phys. Rev. B, 64*, 075414. [13] Horgan B. et al. (2020) *Icarus, 339*, 113526. [14] Murphy A. E. et al. (2020) *Sed. Geol., 410*, 105777. [15] Kouketsu Y. et al. (2014) *Island Arc, 23*, 33-50.