CHALLENGES FACING RAMAN SPECTROSCOPY ON MARS: LESSONS FROM AN EARTH BASED ANALOG.

A. Olcott Marshall[1] and C. P. Marshall[1], [1]Department of Geology, Lindley Hall, 1475 Jayhawk Blvd, University of Kansas, Lawrence, KS, 66045, cpmarshall@ku.edu and olcott@ku.edu

Introduction: Raman spectroscopy can provide chemical information about a sample quickly and non-destructively with little to no sample preparation, making it an ideal instrument for Mars rover missions. The ESA ExoMars planetary mission scheduled for launch in 2018 will contain a miniaturized Raman spectrometer (RLS) as part of the Pasteur payload, and NASA is independently developing miniaturized Raman spectrometers for future Mars missions, including, potentially, the 2020 rover mission. The Raman spectrometers that are being miniaturized for future life-detection missions on Mars have similar spectral parameters to existing field portable and hand-held Raman spectrometers. These field spectrometers offer the ability to test on Earth the robustness of Raman spectroscopy on Mars, allowing a determination of the types of data that can be collected as well as the potential pitfalls of this method. We used a field Raman spectrometer coupled with benchtop measurements to analyze the mineralogy and biosignatures of Mars analog sites, allowing a determination of the types of data that can be collected as well as the potential problems of this approach. Examining the mineralogy of known sample sites as well as the biosignatures present will allow a determination of how reliable a portable Raman spectrometer on Mars would be to characterize the geology as well as the biology of unknown sites.

Mars Geology: The past few Mars missions, both landed and in orbit, have provided us with a wealth of knowledge about the mineralogical content of the Martian surface, which, by extension, has allowed a determination of past Martian environmental conditions. Direct observations from the rovers *Spirit, Opportunity,* and *Curiosity* have revealed the presence of hematite, jarosite, gypsum, halite, and carbonate on Mars [e.g., 1]. These minerals indicate there was a period of time when Mars' water was highly acidic, iron and sulfate-rich, most likely due to the input of volcanic materials. Many believe that these water bodies could have been ephemeral and subject to evapoconcentration [e.g., 2].

Field Raman Spectroscopy: In addition to the ongoing quest to miniaturize Raman spectrometers for space exploration [e.g., 3], portable Raman spectrometers have been developed for use here on Earth. The applications of these portable instruments are wide-ranging, and they are gaining increasing traction in astrobiological studies. Portable Raman spectrometers have been used to investigate carotenoids and other pigment molecules from extant microbes in Martian analogue environments such Antarctica [4], hypersaline environments in the Atacama Desert [5], arid regions in the Tabernas Desert [6], and carbonaceous material within a stromatolite [7]. Additionally, they have been used to investigate nitrogen compounds, both natural and introduced, in a variety of environments [e.g., 8]. However, all of these studies had the shared goal of characterizing biosignatures with Raman spectroscopy, and none did a general mineralogical survey of the field sites.

Mars Analog Field Sites: For this study we have picked two analog environments, one modern and one ancient, both with a similar mineralogy and sedimentology to observed Martian environments.

Nippewalla Group. The middle Permian Nippewalla Group is exposed throughout south-central Kansas and northern Oklahoma. These evaporite rocks were deposited in terrestrial saline pan systems containing saline mud flats and ephemeral saline lakes. Analyses of fluid inclusions present in subsurface cores indicate that the lakes and groundwater from which these rocks precipitated were extremely acidic, perhaps as low as pH < 1. This Group has been suggested to be a good Mars analog on the basis of its mineralogy and sedimentology.

Great Salt Plains. The Great Salt Plains (GSP) of north-central Oklahoma are unvegetated salt plains extending over ~65 km^2. This continental sabkha formed by the interaction of groundwater with the Permian rocks of the Sumner Group. The Sumner Group, like the overlying Nippewalla Formation, is an ancient evaporite deposit full of halite and anhydrite. These minerals are dissolved out by the groundwater, and the resulting brine, which is carried to the surface by artesian flow, is rich in calcium, sodium, sulfate, and carbonate. Due to this brine, halite is precipitated at the surface and gypsum is precipitated right below the surface. In many respects, its mineralogy and sedimentology is similar to that described on Mars. Additionally, large salt flats have described on Mars.

Results: Samples were analyzed at both localities with a DeltaNu Rockhound portable Raman spectrometer with a wavelength of excitation of 785 nm. A variety of mineral textures and colors were selected for analysis at each locality, and representative data are visible in Figures 1 and 2. At Glass Mountain, cleared surfaces and surfaces covered in iron oxide dust, similar to that which covers many of the surfaces on Mars

[9], were analyzed. Interestingly, the iron oxide dust did not obscure the mineralogy of the underlying rock, as we were able to detect gypsum under the ferric coating (Fig 1A), and we were also able to collect spectra of white and black minerals. All three Raman spectra are indicative of gypsum, as all show characteristic bands due to the internal vibration modes of the SO_4^{2-} tetrahedron. The two most diagnostic bands for gypsum are the ν_1 (SO_4^{2-}) symmetric stretching mode with A_g symmetry at 1008 cm^{-1}, and the ν_3 (SO_4^{2-}) antisymmetric stretching mode with B_g symmetry at 1135 cm^{-1}, although the minor ν_2 (SO_4^{2-}) symmetric bending modes with A_g symmetry at 495 and 412 cm^{-1} and ν_4 (SO_4^{2-}) antisymmetric bending modes with B_g symmetry at 672 and 613 cm^{-1} are also characteristic of gypsum. Both of the diagnostic bands (at 1008 and 1135 cm^{-1}) are present in all three of the spectra, and the intensity of the 1008 cm^{-1} band is nearly identical in all three samples (Fig 1A). At GSP, as halite is not Raman active, we collected a spectra of a subsurface selenite crystal by digging slightly below the surface (Fig 2). The diagnostic gypsum bands are also present in this spectrum.

The data collected with a green laser line on samples from Glass Mountain are not as informative as that collected out in the field with the 785 nm source (Fig 1B). There is a great deal of autofluorescence in all of the benchtop data, and the effect is so prominent in the white gypsum that it obscures any bands, rending the white gypsum unanalyzable at this wavelength. The band at 1135 cm^{-1} is barely able to be differentiated from the background signal in both the hematite covered gypsum and in the black gypsum, and, intriguingly, the 1008 cm^{-1} band is of much greater intensity in the covered gypsum than in the uncovered gypsum. Although the bands at 672, 613, 495, and 412 cm^{-1} are resolvable in the black and covered samples, those bands are not, in and of themselves, diagnostic for gypsum. Similarly, the spectrum of selenite from GSP (Fig 2B) is not as informative as that collected out in the field, due to the presence of autofluorescence. Additionally, the 1135 cm^{-1} band is much less pronounced in the 514.5 nm laser excitation wavelength spectrum than it is in the 785 nm laser excitation wavelength spectrum (Fig 2).

Conclusion: These preliminary data suggest that the red (785 nm) laser excitation source is better suited to collecting data from iron- and sulfate-rich environments than the green laser is. Given the interest in Raman spectroscopy for Martian investigation, it is crucial to test wavelengths in a Mars analog environments to determine which excitation wavelength is most suited to collecting data on the iron- and sulfate-rich Martian surface.

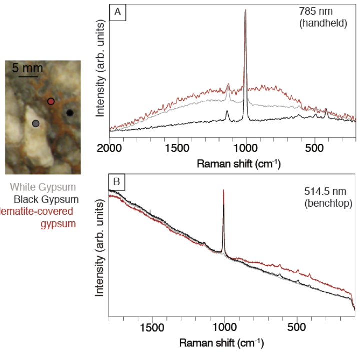

Figure 1: Spectra collected on samples from the Nippewalla Formation using a 785 nm laser excitation line (1A) and a 514.5 nm laser excitation line (1B).

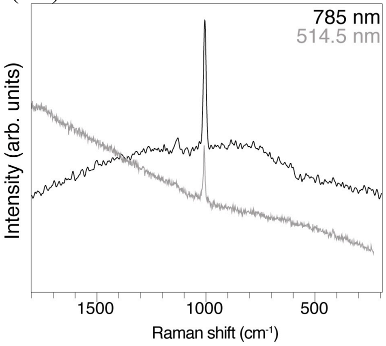

Figure 2: Spectra collected on selenite from the Great Salt Plains using a 785 nm laser excitation line (black line) and a 514.5 nm laser excitation line (grey line).

References: [1] Fairen AG, et al. (2009) *Planet Space Sci* 57, 276–87. [2] Knauth LP, Burt DM, Wohletz KH. (2005) *Nature* 438, 1123–8. [3]Edwards HGM, Hutchinson I, Ingley R. (2012) *Ana Bioanal Chem* 404, 1723–31. [4] Dickensheets DL, Wynn-Williams DD, Edwards HGM, SCHOEN C, CROWDER C, Newton EM. (2000) *Journal of Raman Spectroscopy* 31, 633–5. [5] Vitek P, Jehlicka J, Edwards HGM, Hutchinson I, Ascaso C, Wierzchos J. (2012) *Astrobiology* 12, 1095–9. [6] Miralles II, Jorge-Villar SES, Cantón YY, Domingo FF. (2012) *Astrobiology* 12, 743–53. [7] Olcott Marshall A, Marshall CP. (2013) *Astrobiology* 13, 814-820. [8] Culka AA, Jehlička JJ, Strnad LL. (2012) *Spectrochim Acta A* 86, 347–50. [9] Christensen PR, et al. (2003) *Science* 300, 2056–61.