Limitations on Raman Spectroscopy on Mars: Lessons from Oklahoma A. Olcott Marshall[1] and C.P. Marshall[1], [1]Department of Geology, University of Kansas, 1475 Jayhawk Blvd, Lawrence KS 66045 olcott@ku.edu cpmarshall@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 as part of the Pasteur payload, and NASA has selected two different Raman spectrometers for the 2020 rover mission. We used a field Raman spectrometer similar to those developed for the rovers 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. Our preliminary research indicates collecting Raman spectra on Mars may not be as straight forward as previously assumed, and further instrumental modifications may be needed.

Raman Spectroscopy on Mars: Gypsum minerals have been characterized with Raman spectroscopy in an attempt to better understand the types of data that could be collected by a rover on Mars. However, these tests were all performed on pure gypsum free of trace metal contaminants [1-8]. None of these tests actually provide a good proxy for conditions on Mars, where surficial minerals are coated in iron oxide dust [9] and sulfate minerals are likely to be enriched in trace metals like chromium, which has been found in high concentrations on Mars [10-12].

As chromium is a strong autofluorescent emitter [13], even trace quantities of chromium can produce spectra where the signal to noise ratio is too high to obtain any usable data. Gypsum is known to incorporate chromium ions as it crystallizes [14]. *Curiosity* has measured chromium concentrations as high as 5200 ppm at Gale Crater, with an average concentration of 2984 ppm [15].

SHERLOC, the Raman spectrometer selected to fly on the 2020 Mars mission, will use a deep UV laser excitation source, ostensibly to avoid the issue of fluorescence interference [16-17]. However, chromium oxides are also known to undergo resonant Raman enhancement when excited with deep UV wavelength excitation [18]. Resonance Raman enhancement occurs when the incident laser frequency (here, 248.6 nm), is close to the electronic transition of the molecule being studied (here, 244 nm). This resonance leads to a greatly enhanced intensity of the Raman bands, meaning that trace quantities of the resonantly enhanced material can swamp out the bands produced by other compounds, including any potential biosignatures, like carotenoids, which do not undergo resonance enhancement in the deep UV [19].

Mars Analog: To further explore these potential issues, we have identified two Mars-analog field sites in northern Oklahoma: One consists of a 250-million-year-old sequence of high-chromium semi-arid aeolian (wind-deposited) terrestrial sediments with abundant ancient soils interspersed with evaporative gypsum, limestone, and mudstone beds interpreted to represent ephemeral acidic and saline lakes; the other is a modern continental evaporative lake formed by the interaction of groundwater and the evaporate-rich sequence described above [20]. Both sites have similar mineralogy, sedimentology, and trace element composition to observed Martian environments. Our prelimary data from these sites reveal that it is possible to detect preserved biomarkers in these localities, but not with the instrumental parameters currently selected to go to Mars for the ExoMars mission.

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