IMPLICATIONS OF DEEP UV RAMAN SPECTRA OF GYPSUM AND FE-BEARING DUST MIXTURES FOR GYPSUM DETECTABILITY BY THE SHERLOC M2020 INSTRUMENT. N. C. Haney[1], R. V. Morris[2], R. S. Jakubek[1], M. D. Fries[2]. [1]Jacobs, NASA Johnson Space Center, Houston, TX 77058. [2]NASA, Johnson Space Center, Houston, TX 77058.

Introduction: Key science objectives of the Mars2020 Scanning Habitable Environments with Raman & Luminescence for Organics & Chemicals (SHERLOC) instrument suite include identification and characterization of inorganic and biologic phases and investigation of the past habitability of Jezero crater [1, 2]. To fully interpret in situ data received from SHERLOC, databases of deep ultraviolet (DUV) Raman spectra from a wide variety of martian analogue materials are being developed by us and others [e.g., 3]. Ferrous and ferric iron are abundant on the martian surface in basalt and, depending on alteration and transport processes, its alteration products. Fe-bearing phases are important to characterize with respect to detectability by DUV Raman spectroscopy because they strongly absorb DUV radiation, thereby decreasing Raman peak intensity [3, 4].

Ca-sulfates and Fe-bearing minerals have been commonly detected on the martian surface [5, 6]. In this analogue study, we collected Raman spectra of mechanical mixtures of powders of hematite HMS3 (~120 nm discrete particle diameter [7]), palagonite HWMK919 (<5 µm size fraction [8]) and gypsum WD163 (<150 µm size fraction) to examine the detectability of gypsum in the presence of relatively finer-grained, Fe bearing material. Because of the difference in particle diameters, hematite and palagonite powders act as surrogates for martian dust, coating at small concentrations and then enveloping larger gypsum particles.

Materials and Methods: The two sets of mixtures (HMS3-WD163 and HWMK919-WD163) were each prepared to have 2, 5, 10, 20, 40, and 60 wt.% HMS3 or HWMK919. The gypsum endmember (Wards Scientific, Walton, Nova Scotia, CD) was selected as the Ca-sulfate endmember because of its well characterized Raman spectrum, strong DUV Raman signal with little fluorescence, and stability in laboratory air. The relatively strong DUV Raman spectrum allowed for the effects of iron on resulting spectra to be readily apparent. HMS3 and HWMK919 as martian dust analogues place an upper limit on the effect of Fe-bearing dust on the DUV spectra of gypsum.

A total of 15 samples were analyzed including endmembers WD163, HMS3, and HWMK919. Note that the HMS3 and HWMK919 spectra have no detectable Raman peaks, presumably the result of virtually complete absorption of incident and scattered DUV radiation by the powders. Each powder was individually weighed before adding to a sample vial for a total of ~100 mg per mixture. Each mixture was then sonicated in absolute ethanol and allowed to completely dry before Raman analysis.

Raman spectra were collected on the Analogue Complementary Raman for Operations oN Mars (ACRONM) DUV (248.6 nm) instrument at the NASA Johnson Space Center in the ARES Raman Laboratory. ACRONM is an analogue for the Mars2020 *Perseverance* rover SHERLOC Raman instrument. The incident laser beam is donut in shape with a diameter of ~100 µm. Measurements were conducted in air at ~25°C under ambient pressure conditions and with nominally equivalent instrumental and focusing conditions, enabling comparison of peak amplitudes among samples after scaling to equivalent data acquisition times. All spectra were offset to 100 counts at ~165 cm^{-1}.

Discussion: The amplitude of the endmember WD163 gypsum Raman peak at 1006 cm^{-1} was 3218 counts and the corresponding values for the endmembers at the same Raman shift was 98 counts for HMS3 (Fig. 1) and 105 counts for HWMK919. The Raman peak amplitude decreased with increasing proportions of HWMK919 and reached the value for the endmember for mixtures with ~60 wt.% HWMK919. The Raman peak amplitude rapidly decreased with increasing HMS3 and reached the value for the endmember for mixtures with ~20 wt.% HMS3 (Fig. 2). The difference is attributed to the larger Fe_2O_3T content for HMS3 (~100 wt.% [7]) compared to HWMK919 (<5 µm; 22 wt.% [8])

Summary: DUV Raman spectra for mixtures of gypsum with hematite and palagonitic powders with the latter having maximum discrete particle diameter ~100 to ~30 times smaller than that for the gypsum powder demonstrate that natural or abraded Fe-bearing dust on martian rock surfaces will reduce the intensity of DUV Raman peaks compared to undusted rock surfaces in proportion to the amount of dust and its iron concentration. Furthermore, Fe-bearing dust spectrally equivalent hematite and HWMK919 (<5 µm) without detectable DUV Raman peaks will have no manifestation of its presence in the DUV Raman spectrum of a dusty rock surface.

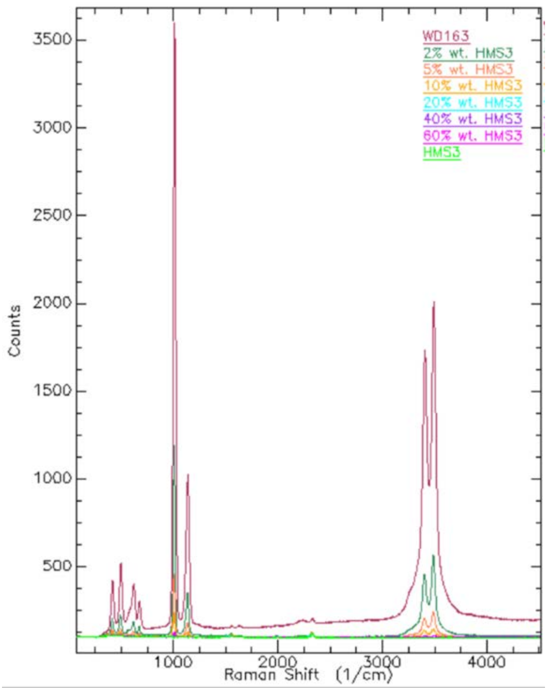

Figure 1. Raman spectra of gypsum (WD163), hematite (HMS3), and their mixtures having 2, 5, 10, 20, 40, and 60 wt.% hematite. A reduction in gypsum Raman peak amplitudes with increasing proportions of hematite.

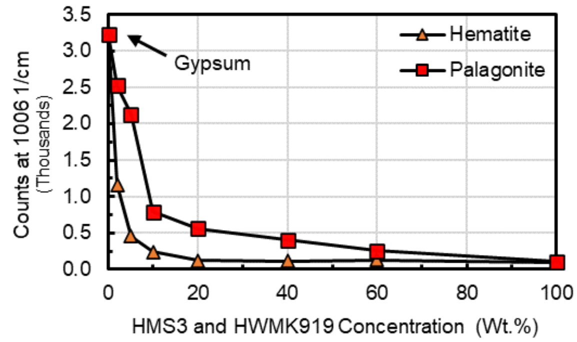

Figure 2. Plot of the intensity of the gypsum Raman peak at 1006 cm^{-1} for gypsum - hematite and gypsum - palagonite mixtures.

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