RELATIVE DETECTABILITY OF IRON-BEARING PHASES FOR THE MARS 2020 SHERLOC DEEP UV RAMAN INSTRUMENT: 1. FOCUSING ON CARBONATES. R. V. Morris[1], N. C. Haney[2], R. S. Jakubek[2], M. D. Fries[1], J. V. Clark[2], L. Le[2], S. A. Mertzman[3]. [1]ARES NASA-JSC, Houston, TX 77058 (richard.v.morris@nasa.gov), [2]Jacobs, ARES NASA-JSC, Houston, TX 77058, [3]Franklin and Marshall College, Lancaster, PA 17603.

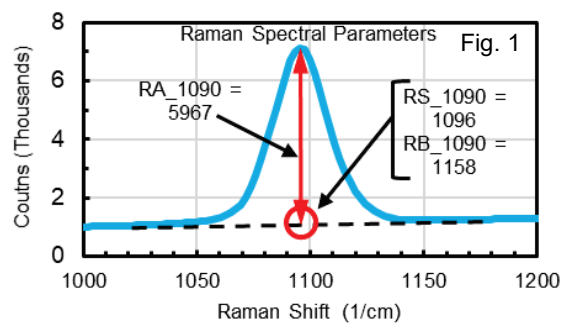
Introduction. A deep ultraviolet (DUV) Raman and fluorescence instrument is a surface standoff instrument mounted on the robotic arm of the Mars 2020 (M2020) rover *Perseverance,* and it is a key element of the Scanning Habitable Environments with Luminescence for Organics and Chemicals (SHERLOC) investigation [1]. Measurement and science objectives include mineralogical and organic images (~100 µm/pixel) that map sub-millimeter spatial distributions and characterization of primary and secondary minerals, potential organics, and their interaction/alteration products. The results of data analysis pertain to understanding igneous and alteration processes on Mars through time, assessing habitability, evidencing in situ biosignatures, and, along with results from other *Perseverance* instruments, selecting samples to cache for Mars sample return.

Acceptance of the SHERLOC investigation for the NASA M2020 mission [2] created a need for Mars-relevant DUV Raman spectra, particularly for inorganic materials [e.g., 3, 4]. As reported previously [e.g., 4 - 6], phases with Fe cations as essential elements (e.g., siderite ($FeCO_3$) and ankerite ($FeCa(CO_3)_2$) for carbonates) significantly hinder their detection by DUV Raman because of intense absorption of incident and scattered DUV laser radiation by Fe cations. We report here the relative detectability of carbonates $(Mg,Ca,Fe,Mn)CO_3$ by DUV Raman using a SHERLOC analog laboratory instrument.

Samples and Methods. We recorded deep ultraviolet (DUV) fluorescence and Raman spectra for 34 naturally occurring and carbonate-bearing samples using the JSC-fabricated Raman instrument (ACRONM: Analogue Complementary Raman for Operations oN Mars). It is a closed-beam laboratory analogue (pulsed Ne-Cu laser at 248.6 nm focused to an ~100 µm spot) of the SHERLOC DUV Raman instrument. Spectra were recorded in laboratory air at room temperature under equivalent instrumental conditions so that peak intensities among samples could be compared after scaling to equivalent spectral acquisition times. Wavenumber calibration was against cyclohexane and the atmospheric N_2 Raman peak (2330 cm^{-1}).

Carbonate-bearing samples from the JSC collection of Mars analog samples included nominal endmemeber compositions (e.g., calcite, magnesite, siderite, and rhodochrosite), $(Ca,Mg,Fe,Mn,Ni)CO_3$ solid solutions, and carbonate-bearing rocks (e.g., carbonate-cemented basalt and carbonaceous chert). All samples were analyzed as powders (<45 µm or <150 µm). Chemical compositions by standard electron probe micro-analysis (EPMA) or X-ray fluorescence (XRF) methods were determined for 17 samples. Samples analyzed by XRF were whole-rock analyses and thus may deviate from actual carbonate compositions.

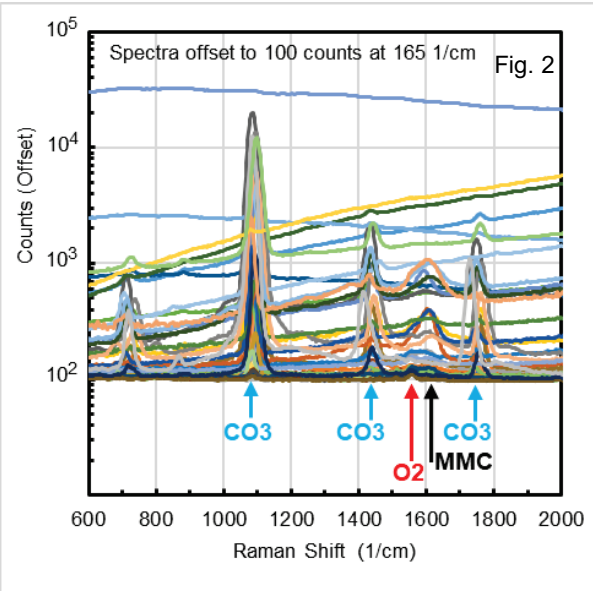
Using the Raman carbonate peak at ~1090 cm^{-1} for a dolomite as an example, we define three spectral parameters (Fig.1): Raman shift (RS_1090), Raman peak amplitude (RA_1090), and Raman peak baseline (RB_1090). The parameter RS_1090 is the actual peak position near 1090 cm^{-1} and normally assigned to carbonate but could result from and/or have contributions from other phases. Because we report our spectra offset to 100 counts at ~165 nm (in order to avoid negative baseline values in semi-log plots), the RB_1090 value in Fig.1 is offset-corrected.

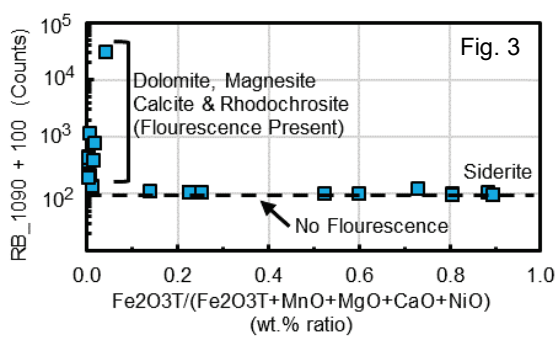


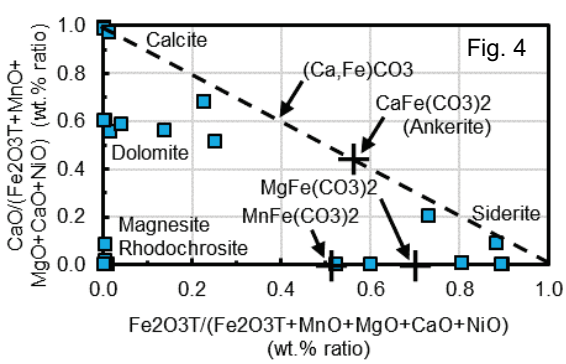
Results and Discussion. The Raman/fluorescence spectra (Fig. 2) over the wavenumber region for the three major carbonate peaks exhibit a wide range in the intensity of Raman carbonate peaks and broad fluorescence spectra. For samples with detectable fluorescence, its intensity either increase or decrease with wavenumber, and for a few samples overwhelmed the Raman spectrum (e.g., uppermost trace in Fig. 2). Present in many samples are also Raman peaks near ~1605 cm^{-1} resulting from macromolecular carbon (MMC) [e.g., 7, 8] and ~1550 cm^{-1} resulting from atmospheric O_2.

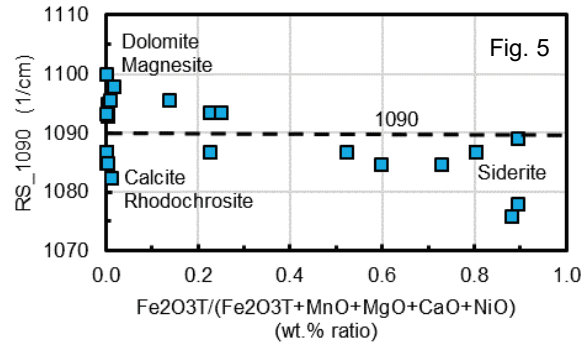
An apparent dependence of fluorescence intensity on Fe concentration is advanced in a plot (Fig. 3) of Raman spectrum baseline for the most intense carbonate peak (RB_1090) versus the fraction of total Fe as Fe_2O_3 (Fe_2O_3T) (oxide ratio in wt.%). The nominally Fe-free endmember carbonates (magnesite ($MgCO_3$, calcite ($CaCO_3$), dolomite $MgCa(CO_3)_2$, and rhodochrosite ($MnCO_3$) with ($Fe_2O_3T/\Sigma(oxides) < 0.011$) have no detectable fluorescence. The lower limit for fluorescence quenching from Fig.3 is ($Fe_2O_3T/\Sigma(oxides) \sim 0.14$. The quenching process is under investigation.

Available chemistry for carbonate bearing samples is summarized in Fig. 4. The subset well represent carbonate endmember compositions and presumptive carbonate solid solutions. The dependence of the Raman shift for most intense carbonate Raman peak (RS_1090) on carbonate composition is investigated in Fig. 5. The data show that Mg-rich carbonates (magnesite and dolomite) have somewhat elevated values for RS_1090 compared to Mg-poor carbonates ((Ca,Fe,Mn)CO_3).

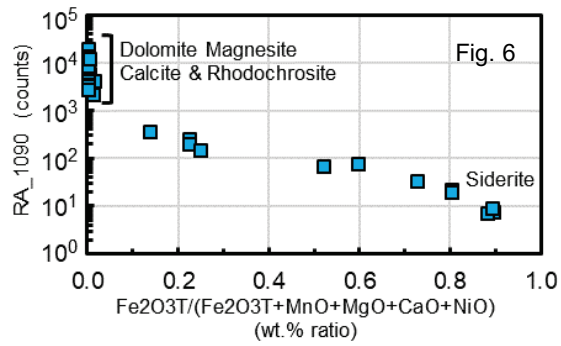








The relative detectability of carbonates as a function of Fe concentration is the primary focus of this effort. The data show, as represented by RA_1090 (Fig 6), that essetially Fe-free carbonates (dolomite, magnesite, calcite, and rhodochrosite) have a higher relative detectability by factors of ~200 to 2000 over their Fe-rich counterpart siderite (RA_1090 ~ 9 counts). In other words, to detect siderite on Mars, a SHERLOC spectrum would need a signal-to-noise ratio favorable to detection of a Raman peak with an amplitude of ~5-9 counts (RA_1090) in broad agreement with [4,5].



Applications to Mars. Fe-rich carbonate has been detected on Mars by the Mössbauer MIMOS-II and Mini-TES instruments at Gusev crater [9] and by the CheMin XRD instrument at Gale crater [10]. The likely scenario for DUV Raman at Jezero crater, because of absorption of UV radiation by Fe cations, is viable detection of Fe-free carbonates and their solid solutions with Fe^{2+} up to some limiting Fe concentration and non-detection of endmember and near-endmember siderite. However, a null detection of siderite by SHERLOC coupled with measurements by other *Perseverance* instruments (e.g., PIXL and SuperCam) could imply the presene of siderite.

References. [1] Bhartia *et al.*, 2021, *SSR, 217,* 1. [2] Beegle *et al.*, 2015, *2015 IEEE Aerospace Conf. Proc.*, 1. [3] Abbey *et al.*, 2017, *Icarus, 290*, 201. [4] Shkolyar *et al.,* 2018, *Astrobilolgy, 18,* 431. [5] Carrier *et al.*, 2019, *JGR, 124*, 2599. [6] Hollis *et al.*, 2021, *Icarus, 357*, 114067. [7] Alexander *et al.*, 1998, *M&PS, 33*, 603. [8] Steele *et al.*, 2012, *Science, 337*, 212. [9] Morris *et al,* 1985, *JGR, 90*, 3126. [10] Bristow *et al.*, 2021, *Science, 373*, 198.