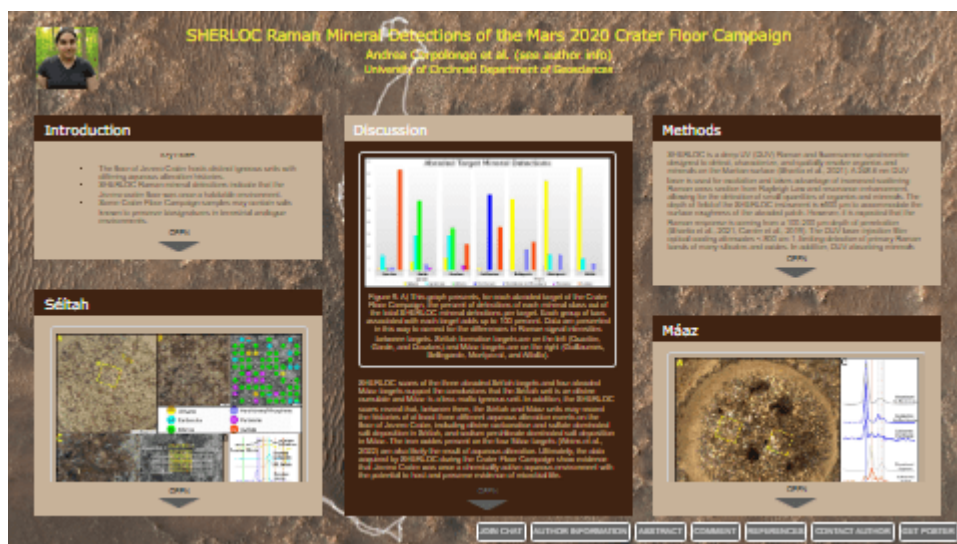


SHERLOC Raman Mineral Detections of the Mars 2020 Crater Floor Campaign



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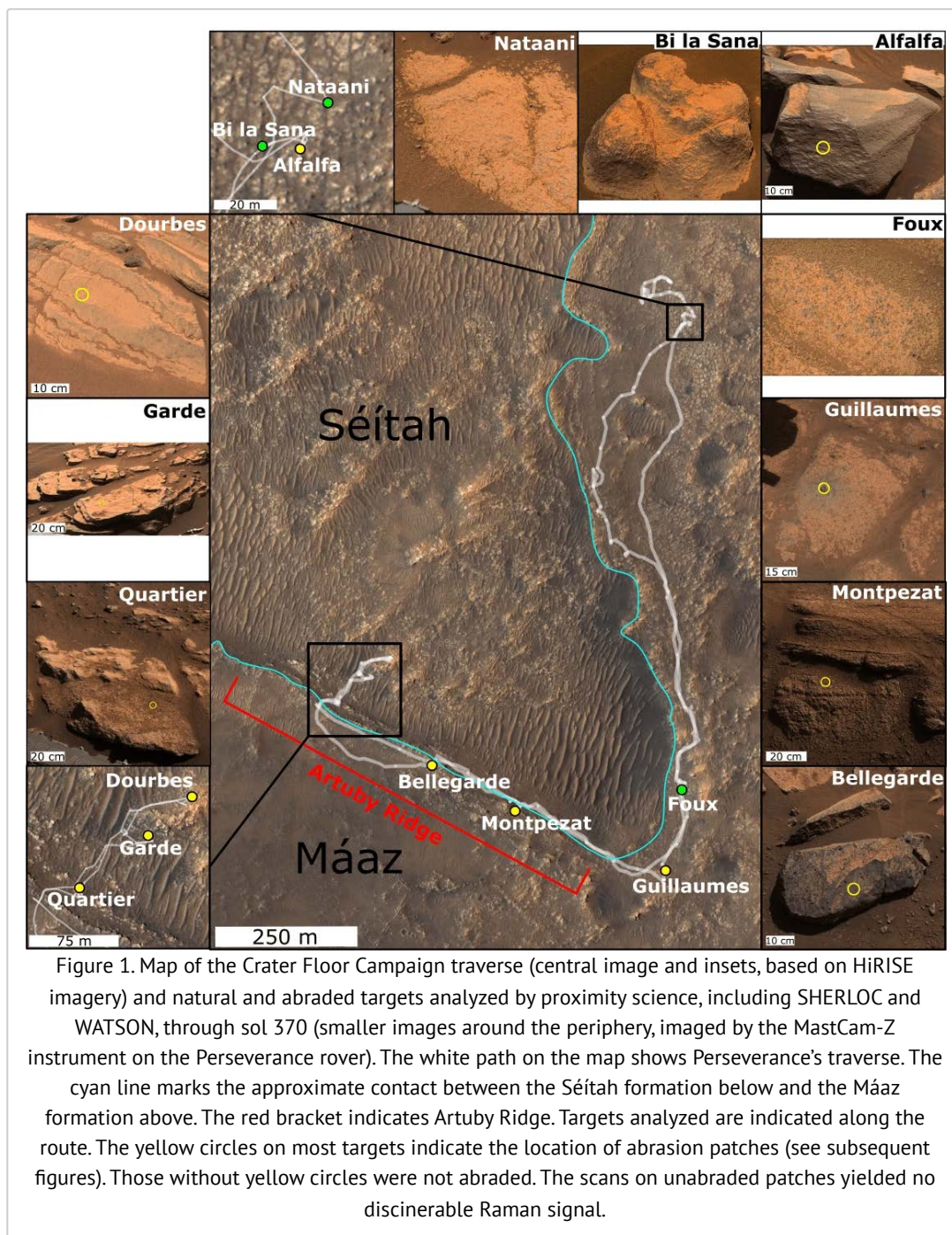
ABSTRACT

During the first science campaign of the Mars 2020 mission, Perseverance rover's Scanning Habitable Environments with Raman and Luminescence for Organics and Chemicals (SHERLOC) deep UV Raman and fluorescence instrument collected microscale, two-dimensional Raman and fluorescence images on ten natural and abraded targets on two different Jezero crater floor units: Séítah and Máaz. SHERLOC Raman images collected during the Crater Floor Campaign indicate that Séítah and Máaz are mineralogically distinct igneous units with complex aqueous alteration histories. SHERLOC data show that Séítah is olivine-rich with evidence of olivine carbonation, while Máaz features widespread silicates, but lacks olivine. Both units feature salt deposits. In Séítah, the salts are predominantly sulfate. Where salts are observed in Máaz, they are a mixture of sodium perchlorate and sulfates. Taken together, SHERLOC data collected during the Crater Floor Campaign suggest that the Jezero crater floor once hosted an environment capable of supporting microbial life and preserving evidence of that life, if it existed.

INTRODUCTION

Key Points

- The floor of Jezero Crater hosts distinct igneous units with differing aqueous alteration histories.
- SHERLOC Raman mineral detections indicate that the Jezero crater floor was once a habitable environment.
- Some Crater Floor Campaign samples may contain salts known to preserve biosignatures in terrestrial analogue environments.



The Crater Floor Campaign was an exploration of the floor of Jezero crater (Sun et al., 2022; Fig. 1). During this campaign, the rover investigated two major units, Séítah and Máaz, which had been identified from orbital data before surface operations commenced (Stack et al., 2020). The older unit, Séítah, previously referred to as the Crater Floor Fractured 1 (CF-F-1) Unit, is light-toned, ridged, and fractured. Séítah is overlain by Máaz, previously referred to as the Crater Floor Fractured Rough (CF-Fr) Unit, which is light-toned and polygonally fractured. Results from the Perseverance payload during the Crater Floor Campaign indicate that both Máaz and Séítah are igneous in origin (Horgan et al., 2022). Máaz is characterized by the presence of abundant pyroxene (Schmidt et al., 2022; Udry et al., 2022), while Séítah is an olivine cumulate (Brown et al., 2022; Farley et al., 2022; Liu et al., 2022; Nuñez et al., 2022; Wiens et al., 2022). The transition between the Séítah and Máaz units is highlighted in cyan in Figure 1.

The Crater Floor Campaign addressed several objectives of the Mars 2020 mission by contributing to a scientific understanding of the geology of Jezero crater, seeking rocks with a high probability of preserving ancient biosignatures and looking for potential biosignatures within rocks of the Séítah and Máaz units, and documenting the geological context of the first set of samples collected for possible future return to Earth. This poster presents spectral maps collected by SHERLOC (Scanning Habitable Environments with Raman and Luminescence for Organics and Chemicals), an arm mounted deep UV (DUV) Raman spectrometer (Bhartia et al., 2021). The maps are paired with high resolution (10.1 $\mu\text{m}/\text{pixel}$) grayscale images collected by the co-boresighted Autofocus Context Imager (ACI), enabling mapping of the location where each Raman spectrum was collected on the target surface. In addition, the Wide Angle Topographic Sensor for Operations and eNginneering camera (WATSON) provides macro-scale, color images of the Raman scan targets. Combining the image color of WATSON images with the high resolution of the ACI images produces colorized ACI images that can allow for the identification of individual mineral grains.

SÉITAH

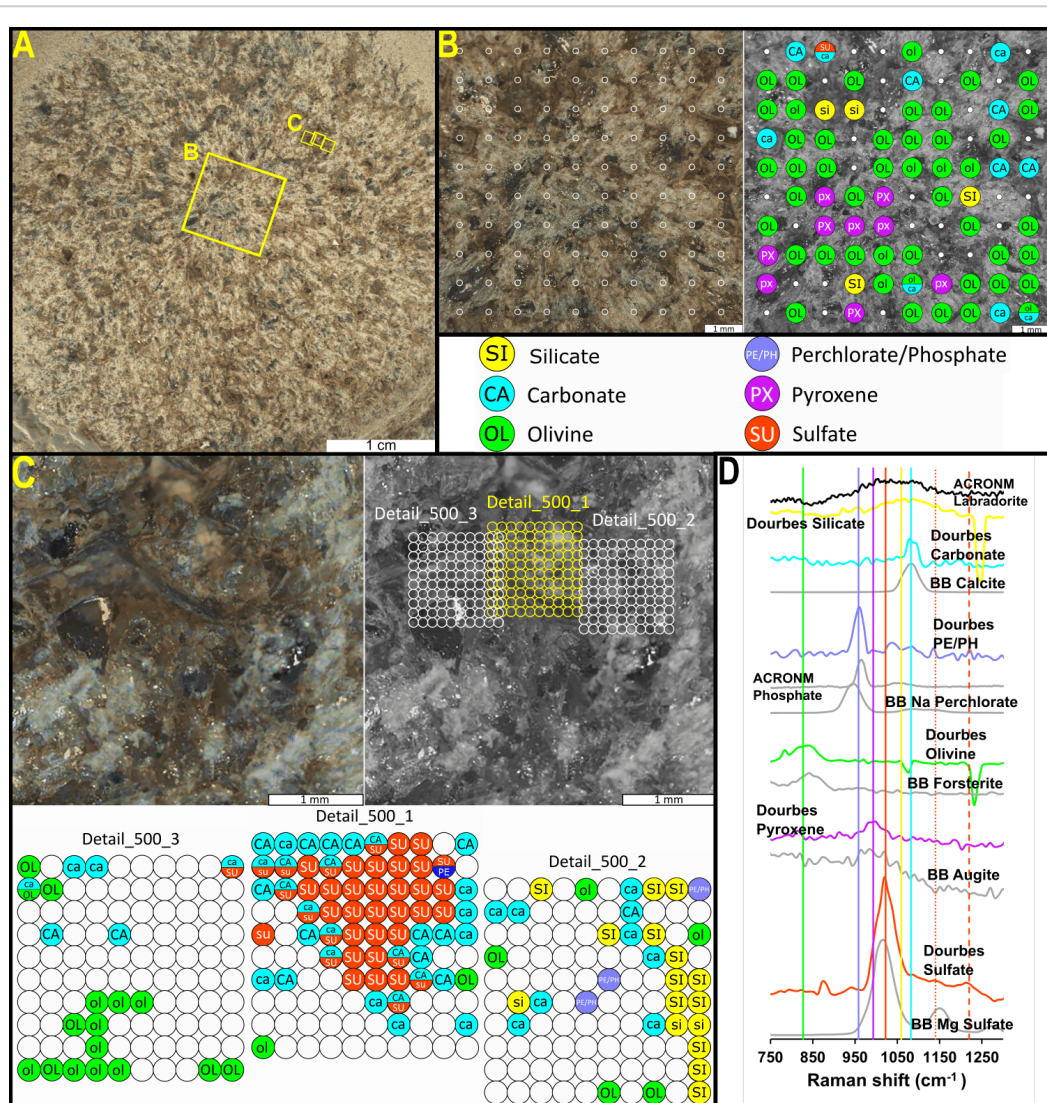


Figure 2. SHERLOC Raman mineral identifications from Dourbes.

A) The abrasion patch imaged by WATSON (image ID

SI1_0257_0689775622_738FDR_N0080000SRCL00006_000095J01). Yellow boxes indicate the location of the scans performed. B) Colorized (left) and grayscale (right) ACI images (image ID SC3_0257_0689786306_125FDR_N0080000SRCL11421_0000LMJ01) of the region of the abrasion patch bounded by the larger yellow box in panel A. The white circles in panel B indicate the locations of SHERLOC analysis spots. Mineral identifications are indicated in the right panel. C) Colorized (left) and grayscale (right) ACI images (image ID

SC3_0269_0690851147_347FDR_N0080000SRCL11373_0000LMJ02) of the region of the abrasion patch bounded by the smaller yellow boxes in panel A. The white and yellow circles in the upper right subpanel of panel C indicate the locations of SHERLOC analysis spots for three 1 mm² Detail scans.

The lower three subpanels show mineral identifications for these three Detail scans. D) Representative Raman spectra of minerals detected with high confidence from the abrasion patch and spectra of mineral standards collected on the SHERLOC Brassboard instrument at JPL and the ACRONM instrument at JSC. Vertical lines indicate peak centers. Spectra are offset along the y-axis for clarity.

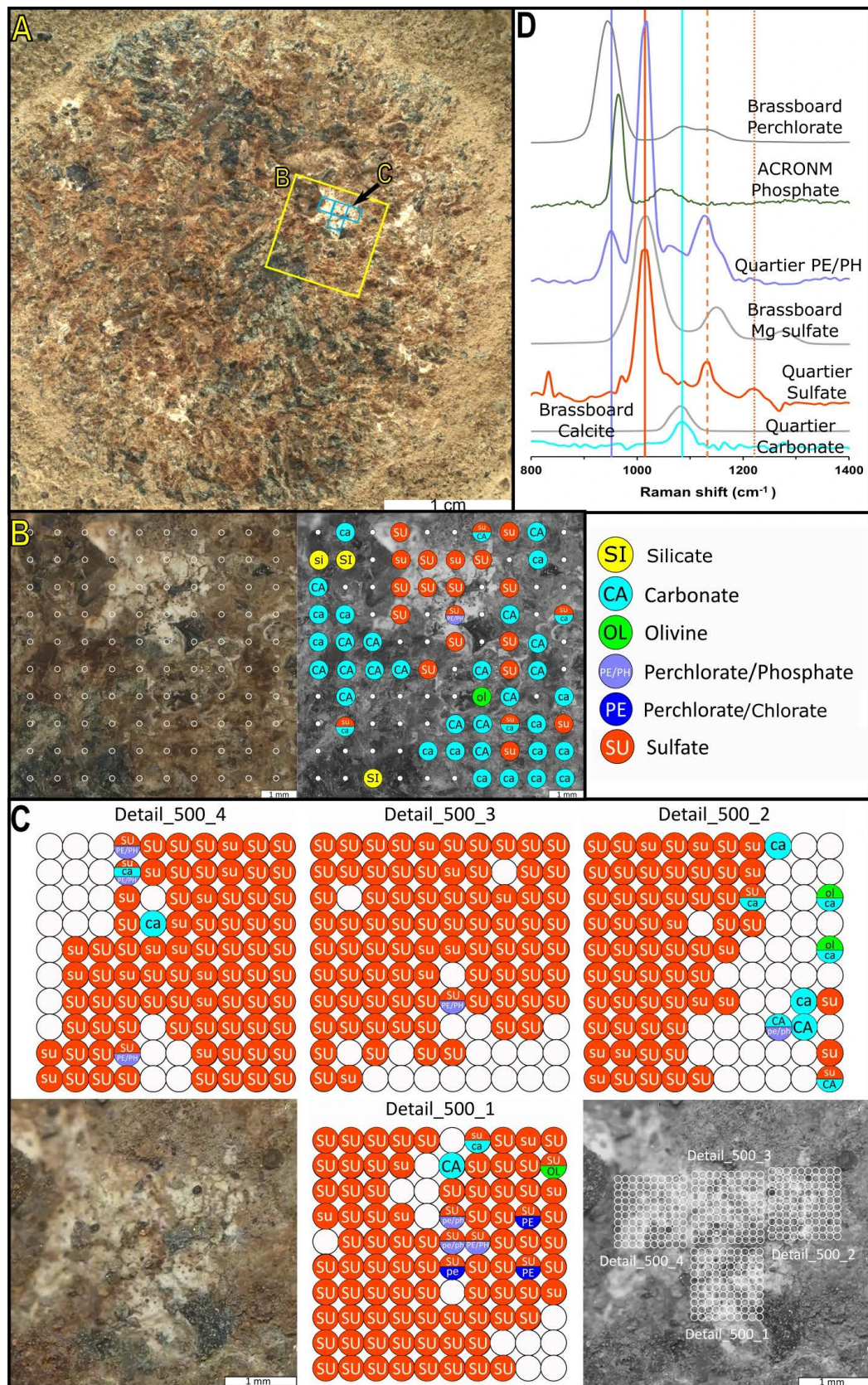
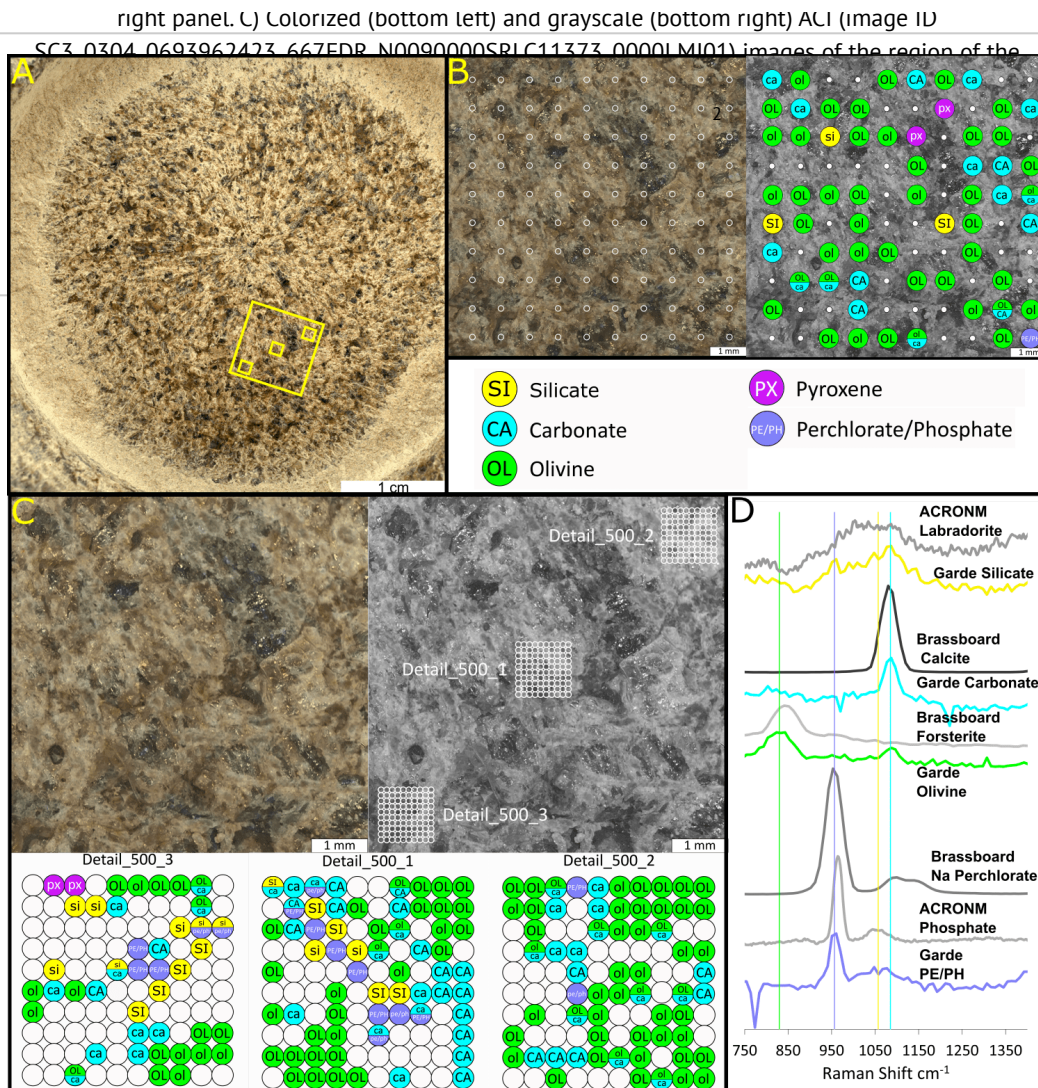
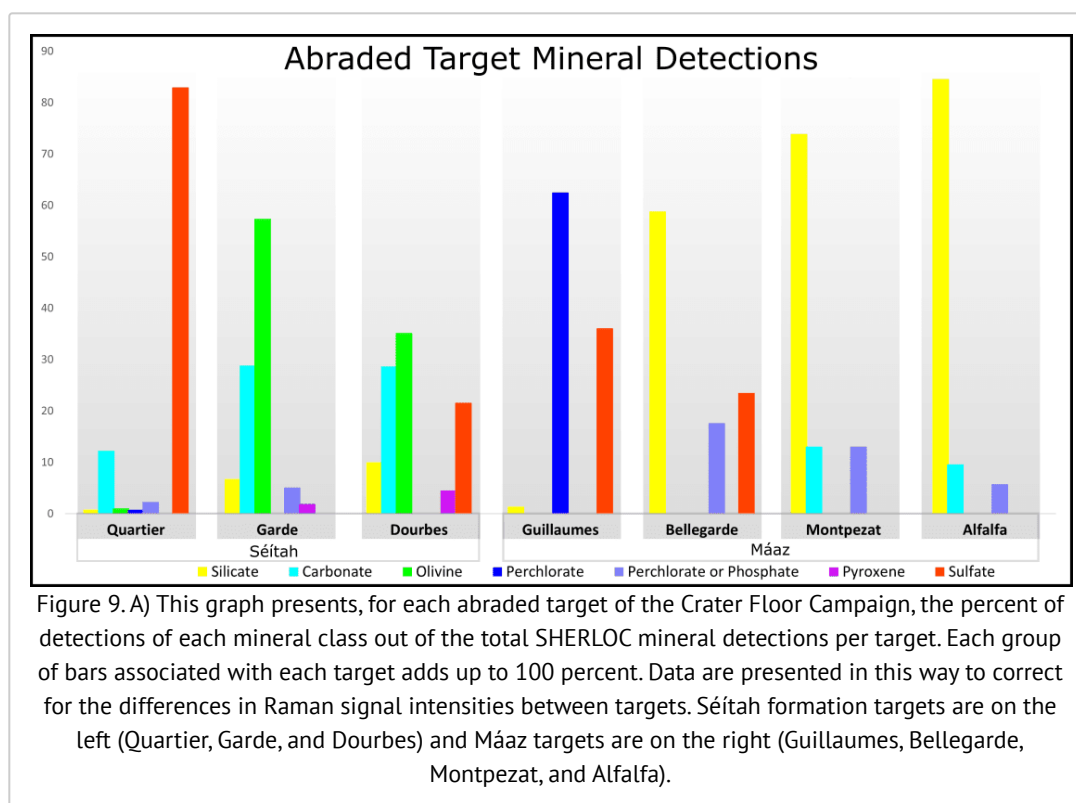


Figure 4. SHERLOC Raman mineral identifications from Quartier. A) The abrasion patch imaged by WATSON (image ID SIF_0292_0692866773_550FDR_N0090000SRCL00702_0000LMJ01). The yellow box indicates the location of the HDR scan and blue boxes indicate the location of the Detail scans.

B) Colorized (left) and grayscale (right) ACI images (image ID SC3_0293_0692982585_671FDR_N0090000SRCL10600_0000LMJ01) of the region of the abrasion patch bounded by the larger yellow box in panel A. The white circles in panel B indicate the locations of SHERLOC analysis spots for 0293_Quartier HDR_500_1. Mineral identifications are indicated in the



DISCUSSION



SHERLOC scans of the three abraded Séítah targets and four abraded Mááz targets support the conclusions that the Séítah unit is an olivine cumulate and Mááz is a less mafic igneous unit. In addition, the SHERLOC scans reveal that, between them, the Séítah and Mááz units may record the histories of at least three different aqueous alteration events on the floor of Jezero Crater, including olivine carbonation and sulfate dominated salt deposition in Séítah, and sodium perchlorate dominated salt deposition in Mááz. The iron oxides present on the four Mááz targets (Weins et al., 2022) are also likely the result of aqueous alteration. Ultimately, the data acquired by SHERLOC during the Crater Floor Campaign show evidence that Jezero Crater was once a chemically active aqueous environment with the potential to host and preserve evidence of microbial life.

Figure 9 shows that the three most common mineral class detections in SHERLOC scans of Séítah targets were olivine, carbonate, and sulfate. Olivine and carbonate detections dominated scans in targets Dourbes and Garde, while minimal olivine was detected in Quartier. Scans of Quartier and Dourbes both revealed patches of sulfate, while Garde scans detected no sulfate. The minimal olivine detections in Quartier and lack of sulfate detection in Garde may not reflect a major difference in the mineralogy of these targets. The discrepancies may, instead, reflect the SHERLOC team's decision to focus Quartier scans on the bright white patches of the target and the patchy nature of salt deposits in the Séítah formation.

We observe gray grains similar to the one that corresponds with a definitive olivine spectrum in 0304_Quartier Detail_500_1 across the surface of Quartier, sometimes rimmed by light reddish-brown material (Fig. 4A). These gray grains appear similar to grains identified as olivine in Dourbes and Garde and the reddish-brown material looks similar to carbonate that was associated with the olivine in Dourbes and Garde (Figs. 2, 3). While it is possible that Bastide, the outcrop that hosted the Garde abrasion (Fig. 1), contains no sulfate deposits, it is equally likely that the Garde abrasion and scans simply did not sample Bastide's sulfate deposits. As demonstrated by the sulfate detected in Dourbes (Fig. 2), Séítah sulfate deposits are not all as visually prominent as the sulfate detected in Quartier (Figs. 4).

The closely associated olivine and carbonate detections in Garde and Dourbes suggest that the olivine cumulate Séítah unit was exposed to at least one aqueous alteration event, during which partial carbonation of olivine took place (Figs. 2 and 3). In particular, detail maps of Dourbes reveal a euhedral olivine crystal with no directly associated carbonate sitting less than one millimeter away from a subhedral olivine grain with adjacent carbonate grains (Fig. 2C). Sulfate deposits in

both Dourbes and Quartier are rimmed by carbonate that is both spectrally and morphologically similar to the carbonate associated with olivine in Dourbes and Garde (Figs. 2, 3, 4). This suggests that all of the carbonates in Séítah formed via the same process, olivine carbonation, and that Séítah's sulfate was deposited later by a sulfate-rich brine, in pore space generated during olivine carbonation through cracking caused by the pressure of carbonate crystal formation (e.g., Xing et al., 2018).

Farley et al. (2022) report that the totality of data collected during the Mars 2020 Crater Floor campaign indicates that the Máaz and Séítah units either originated from two different sources or represent different layers of a single differentiated magma body. The different rock-forming mineral detections of (non- olivine or pyroxene) silicate in the Máaz targets Bellegarde, Montpezat, and Alfalfa, and olivine and pyroxene detections in Séítah targets further supports Farley et al.'s interpretation (Fig. 9). SHERLOC's microscale mapping of Máaz targets reveals that similar spectra assigned to silicate correspond to grains with very different morphologies. Silicate detections in Montpezat and Bellegarde map to sub-millimeter dark blue-gray grains; in Alfalfa, the detections correspond to mm-scale reflective white lathe-like crystals (Figs. 6-8). Although the (non- olivine or pyroxene) silicate spectra reported above were all compared to the same standard labradorite spectrum, the broad bands that led us to assign the spectra to silicate are centered at different wavenumbers: 1050 cm⁻¹, 1036 cm⁻¹, and 1053 cm⁻¹ in Montpezat, Bellegarde, and Alfalfa, respectively. The variable grain morphology and Raman band placement in Máaz silicate detections suggests that they correspond to at least two different silicate mineral species.

Perchlorate and sulfate detected in Guillaumes and Bellegarde scans are evidence of a third possible aqueous alteration event on the floor of Jezero Crater. While the Guillaumes and Bellegarde salt deposits are similar in morphology to the deposits in Dourbes and Quartier, they differ in mineralogy. The deposits in Dourbes and Quartier were predominantly sulfate, with only minor perchlorate contributions. In contrast, SHERLOC mineral detections on the white patch of minerals in Guillaumes were dominated by perchlorate that can, in some cases, be identified as sodium perchlorate, with lesser, but still significant, sulfate contributions. SHERLOC scans of Bellegarde detected sulfate signatures alongside perchlorate or phosphate signatures and SuperCam detected a sodium perchlorate signature (Meslin et al., 2022). Taken together, these SHERLOC and PIXL detections suggest that the salts in Guillaumes and Bellegarde precipitated from a perchlorate-sulfate-bearing brine as it percolated through the Máaz formation rocks.

The mineral detections discussed above are consistent with a changing, habitable aqueous environment that was capable of supporting microbial life and preserving evidence of that life, if it existed. In low-temperature terrestrial environments, carbonation of mafic to ultramafic rocks, which SHERLOC data from Séítah formation targets indicate occurred in the Jezero Crater lake, produces hydrogen that can fuel low-density microbial communities (e.g. Fones et al., 2019; Twing et al., 2017; Woycheese et al., 2015). Terrestrial sulfate and perchlorate brines, similar to the brines that likely deposited the sulfate and perchlorate that SHERLOC detected in Jezero Crater, can host microbial life (e.g., Cesur et al., 2022; Fox-Powell & Cockell., 2018; Heinz et al., 2019, 2020). Furthermore, terrestrial sulfate minerals can trap and preserve organic molecules within their structure (eg., Aubrey et al, 2006; Kotler et al., 2008; Schopf et al., 2012; Shkolyar and Farmer, 2018), and halite- and perchlorate-rich hypersaline subsurface deposits in the Atacama Desert can preserve organic molecules for millions of years (Fernández-Remolar et al., 2013).

METHODS

SHERLOC is a deep UV (DUV) Raman and fluorescence spectrometer designed to detect, characterize, and spatially resolve organics and minerals on the Martian surface (Bhartia et al., 2021). A 248.6 nm DUV laser is used for excitation and takes advantage of increased scattering Raman cross section from Rayleigh Law and resonance enhancement, allowing for the detection of small quantities of organics and minerals. The depth of field of the SHERLOC instrument is ± 500 μm to accommodate the surface roughness of the abraded patch. However, it is expected that the Raman response is coming from a 100–200 μm depth of penetration (Bhartia et al., 2021; Carrier et al., 2019). The DUV laser-injection filter optical coating attenuates < 800 cm^{-1} , limiting detection of primary Raman bands of many silicates and oxides. In addition, DUV absorbing minerals (i.e., some Fe containing minerals) can attenuate the depth of penetration into a material and reduce signal to noise ratios (SNR) (Morris et al., 2022; Razzell Hollis et al., 2021a).

SHERLOC is an arm-mounted instrument, which allows it to be moved into proximity of an analysis target. With no change in arm position, an internal scanning mirror rasters the DUV laser beam across the sample surface. With a maximum area of 7 x 7 mm, Raman/fluorescence spectra are acquired at discrete points with a beam diameter of ~ 100 μm (Bhartia et al., 2021). Prior to each spectrum scan, the Autofocus Context Imager (ACI) is used to acquire 10.1 $\mu\text{m}/\text{pixel}$ resolution grayscale images of the target surface. This provides context for the spectral maps and is used to focus the spectrometer/laser. Color images acquired by WATSON have a spatial resolution ranging from 16 to 150 $\mu\text{m}/\text{pixel}$ and are used for targeting SHERLOC observations and textural analysis (Bhartia et al., 2021; Edgett et al., 2012). SHERLOC is designed to simultaneously collect Raman and fluorescence data on the same CCD with a single readout. To reduce noise, the CCD readout is binned into 3 regions, a Raman region ~ 800 to 4000 cm^{-1} (250 to 273 nm) and two fluorescence regions (274 to 337 and 338 to ~ 370 nm). Each region has a separate wavenumber calibration, previously discussed in detail (Uckert et al., 2021).

Scan Procedures

We use the following nomenclature to describe SHERLOC Raman measurements (Fig. S1). A “target” refers to the specific rock or abraded patch on which data were collected, such as “Nataani” or “Guillaumes,” while a “scan” refers to a specific Raman hyperspectral map that was collected on a target. Each Raman scan is named using the nomenclature “#0001_name_#2_#3”, wherein #0001 denotes the sol on which the scan was performed, name refers to the target and describes the parameters of the scan, #2 is the laser pulses per each point spectrum within a scan, and #3 is the scan number used to differentiate between multiple scans of the same parameter made on the same sol. Each individual spectrum within a scan is referred to as a “point,” and each point within a scan is assigned a number according to the order it occurred in the scan. The first Raman spectra collected within a scan falls at the upper left corner of the hyperspectral map. Collection continues in a serpentine pattern, such that the final spectra in a 100 point scan falls at the lower left corner of the map. High Dynamic Range (HDR) scans consist of 100 points with 780 μm spacing for an image size of 7 x 7 mm. Detail scans consist of 100 points with 100 μm spacing for an image size of 1 x 1 mm. Survey scans consist of 1296 points with fixed spacing between them (50, 144, or 200 μm , depending on the scan template) and 10 or 15 pulses per point. For example, the scan name “0083_Nataani HDR_50_1” describes the first HDR scan performed on Nataani using 50 pulses per point on sol 83 of the Mars 2020 mission.

For each scan SHERLOC performs, single spectra are obtained by first collecting a dark spectrum with no incident laser light and then collecting the active spectrum with the laser firing. The dark scan is then subtracted from the active spectrum to produce the reported Raman spectrum. SHERLOC spectra have a ~ 10 $\text{cm}^{-1}/\text{pixel}$ resolution with a Raman spectral range of ~ 800 – 4000 cm^{-1} . The potential to observe Raman bands in the spectral range below 800 cm^{-1} is limited because SHERLOC’s laser-injection filter has reduced transmission in this region and the 252.9 nm laser plasma line is observed at ~ 650 cm^{-1} . However, very strong bands below 800 cm^{-1} can be observed (Bhartia et al., 2021; Uckert et al., 2021; Razzell Hollis et al., 2021a).

We performed scans on both natural and abraded targets. Targets were abraded using Perseverance’s Rock Abrasion Tool (RAT), which is ~ 45 mm in diameter and capable of creating smooth-bottomed abraded patches up to ~ 1 cm deep. After abrasion, abraded patches are cleaned of dust and cuttings by the gaseous dust removal tool (gDRT), which blasts the abraded target with a high-velocity jet of nitrogen gas (Farley et al., 2020; Moeller et al., 2021). The targets described below as abraded targets were abraded and cleaned as described prior to scanning. Any targets described below as natural targets were neither abraded nor cleaned with the gDRT prior to scanning.

Data Analysis Procedures

We examined each individual Raman spectrum in each scan. We considered any band with a FWHM of 30 cm^{-1} (~ 3 pixels) or more a potential Raman signal. We assigned each single spectrum containing observable Raman signals to its respective mineral class via comparison to standard spectra obtained through laboratory measurements with the SHERLOC Brassboard instrument, an analogue DUV Raman and fluorescence instrument housed at the NASA Jet Propulsion Laboratory (described in detail by Razzell-Hollis et al., 2021a,b) and ACRONM (Analogue Complementary Raman for Operations on Mars). All peak centers were determined with a Gaussian fit function, through the open-source peak fitting software Fityk (version 1.3.1; Wojdyr, 2010).

We display the SHERLOC Raman data through Raman spectral assignments overlain on each scan's associated ACI image. These spectral assignment maps are accompanied by colorized ACI images overlaid with white rings that indicate the location of each point in the scan. The spectral positioning calculations were validated from images of ACI calibration measurements where dust mobilization could be observed. Spectral map/ACI overlays are accurate to within $\sim 44 \mu\text{m}$ near the center of maps, and within $115 \mu\text{m}$ at the $7 \times 7 \text{ mm}$ map corners in the HDR overlays. The points at the start of each scan (scans start at the upper left corner) have less location uncertainty than points at the end of the map scan because of robotic arm drift, which can add up to $\sim 30 \mu\text{m}$ of uncertainty. Each laser shot hits the scanned surface as an annulus $\sim 100 \mu\text{m}$ in diameter. The white rings overlying the colorized ACI images are $\sim 200 \mu\text{m}$ in diameter so that the location being analyzed is visible.

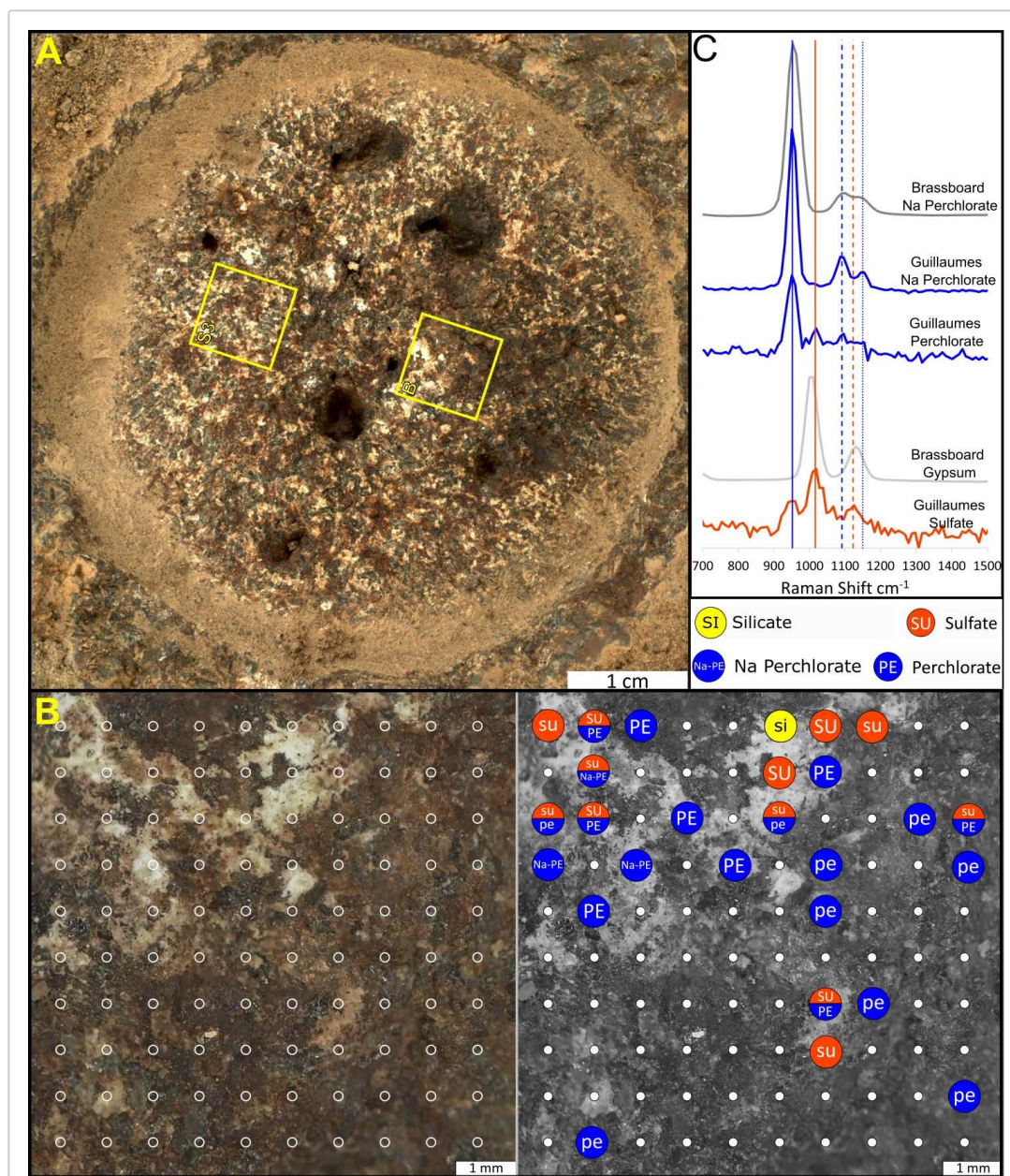
Spectra Signal-to-Noise Analysis

In order to quantitatively assign confidence to SHERLOC mineral detections, we developed a statistical procedure involving comparing apparent signal intensities to a calculated median root-mean-squared-deviation (RMSD) of the noise for each scan. We first calculated the noise RMSD in the 2500–3000 cm^{-1} region of Raman spectra for every individual spectrum in each scan. This “silent” region was selected for its lack of signal in any spectrum, excluding cosmic ray artifacts. Then we determined the median of the noise RMSD values for each scan. We used the median to avoid contributions from any RMSD values that were inflated by cosmic rays, background fluorescence, and other spectral effects. The RMSD noise values differed between Raman images but generally occur in the 20–50 count range.

We designated single spectra Raman bands with intensities $\geq 3X$ the noise RMSD as statistically significant signals. This designation criterion is based on the International Union of Pure and Applied Chemistry's limit of detection for the probability of a data point being statistically above a normally distributed noise background (McNaught & Wilkinson, 1997). The peak position error for SHERLOC Raman bands with intensities $\geq 3X$ the noise RMSD is $\leq \pm 4.0 \text{ cm}^{-1}$. In most instances, we used mean spectra to assign detections to mineral classes. By doing so, we obtained spectra with peak intensities $\geq 10X$ the noise RMSD, which have a peak position error of $< \pm 1 \text{ cm}^{-1}$.

In the context of this poster, signals with $\geq 3X$ the noise RMSD are qualitatively observed with high confidence while those $< 3X$ are observed with less confidence. For these reasons, in the ACI-Raman maps in the poster, we differentiate between Raman signals $\geq 3X$ and $< 3X$ the RMSD noise as a first-order indicator of the assignment confidence. To make this distinction, we label assignments made based on Raman signals $\geq 3X$ the noise with capital letters and those made based on signals $< 3X$ the noise with lowercase letters.

MÁAZ



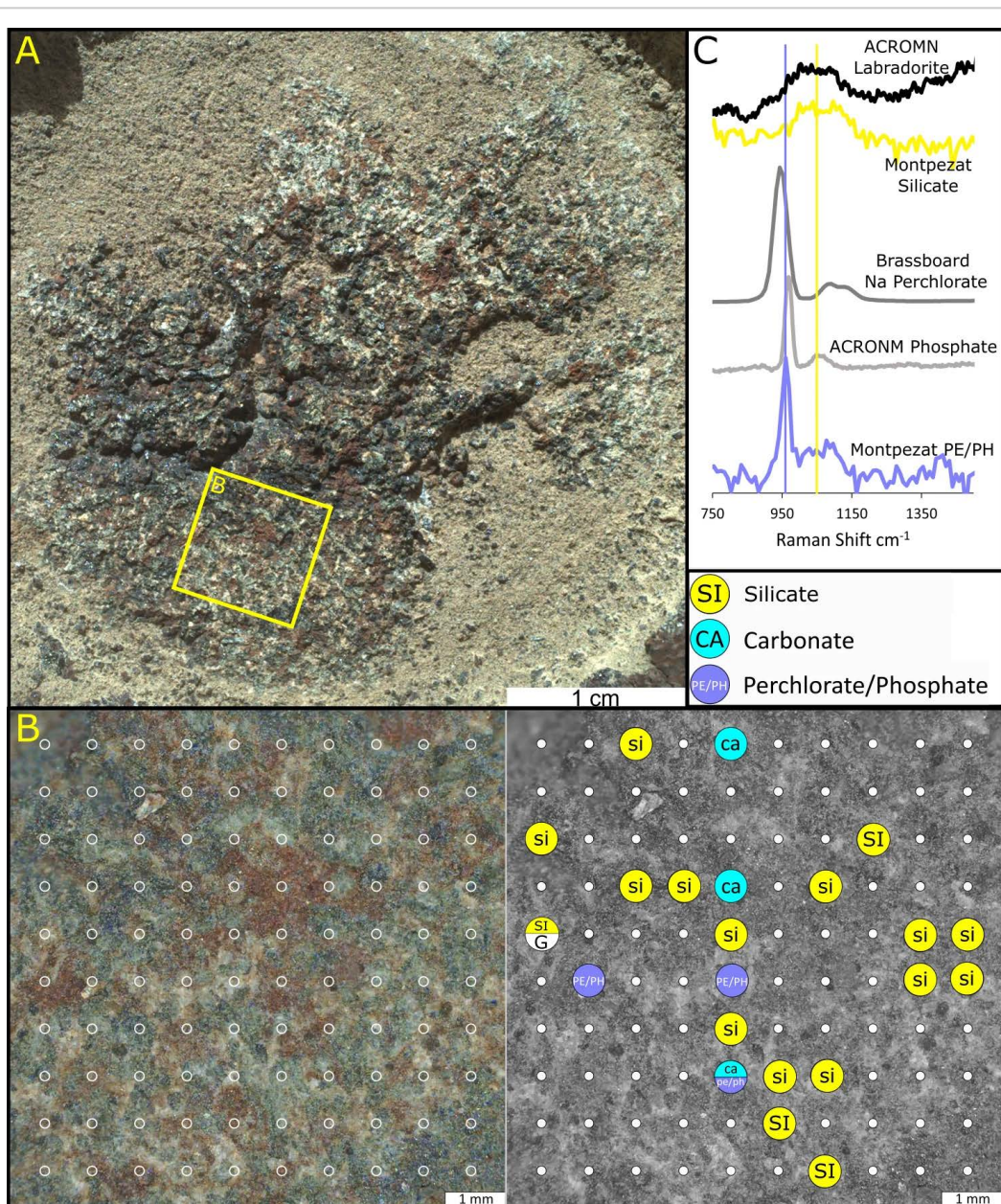
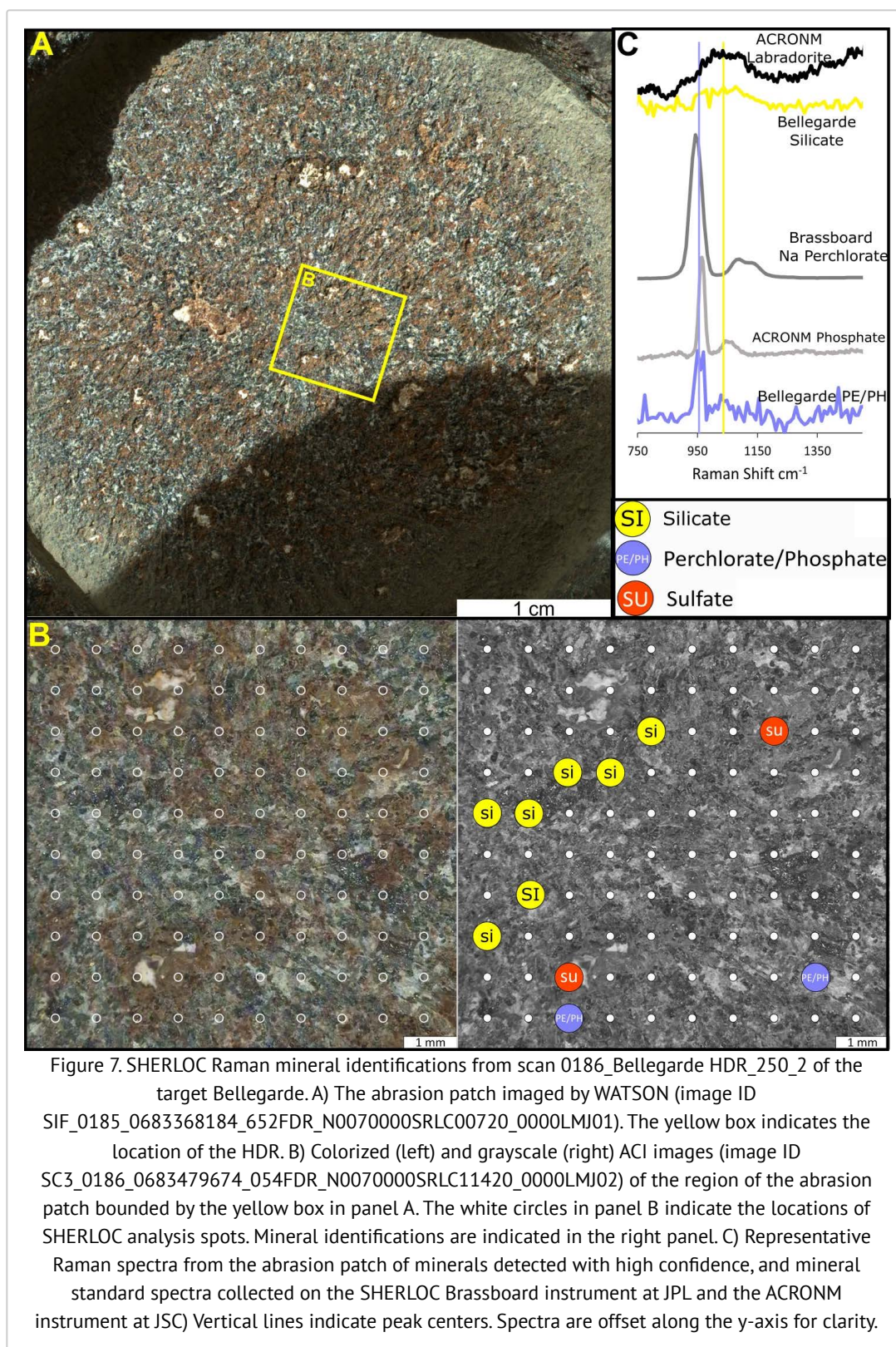


Figure 6. SHERLOC Raman mineral identifications from the 0349_Montpezat HDR_500_1 scan of target Montpezat. A) The abrasion patch imaged by WATSON (image ID SIF_0346_0697661461_972FDR_N0092982SRLC01034_0000LMJ01). The yellow box indicates the location of the scan. B) Colorized (left) and grayscale (right) ACI images (image ID SC3_0349_0697954126_179FDR_N0092982SRLC10600_0000LMJ01) of the region of the abrasion patch bounded by the yellow box in panel A. The white circles in panel B indicate the locations of SHERLOC analysis spots. Mineral identifications are indicated in the right panel. C) Representative Raman spectra from the abrasion patch of minerals detected with high confidence, and mineral standard spectra collected on the SHERLOC Brassboard instrument at JPL and the ACRONM instrument at JSC. Spectra are offset along the y-axis for clarity.



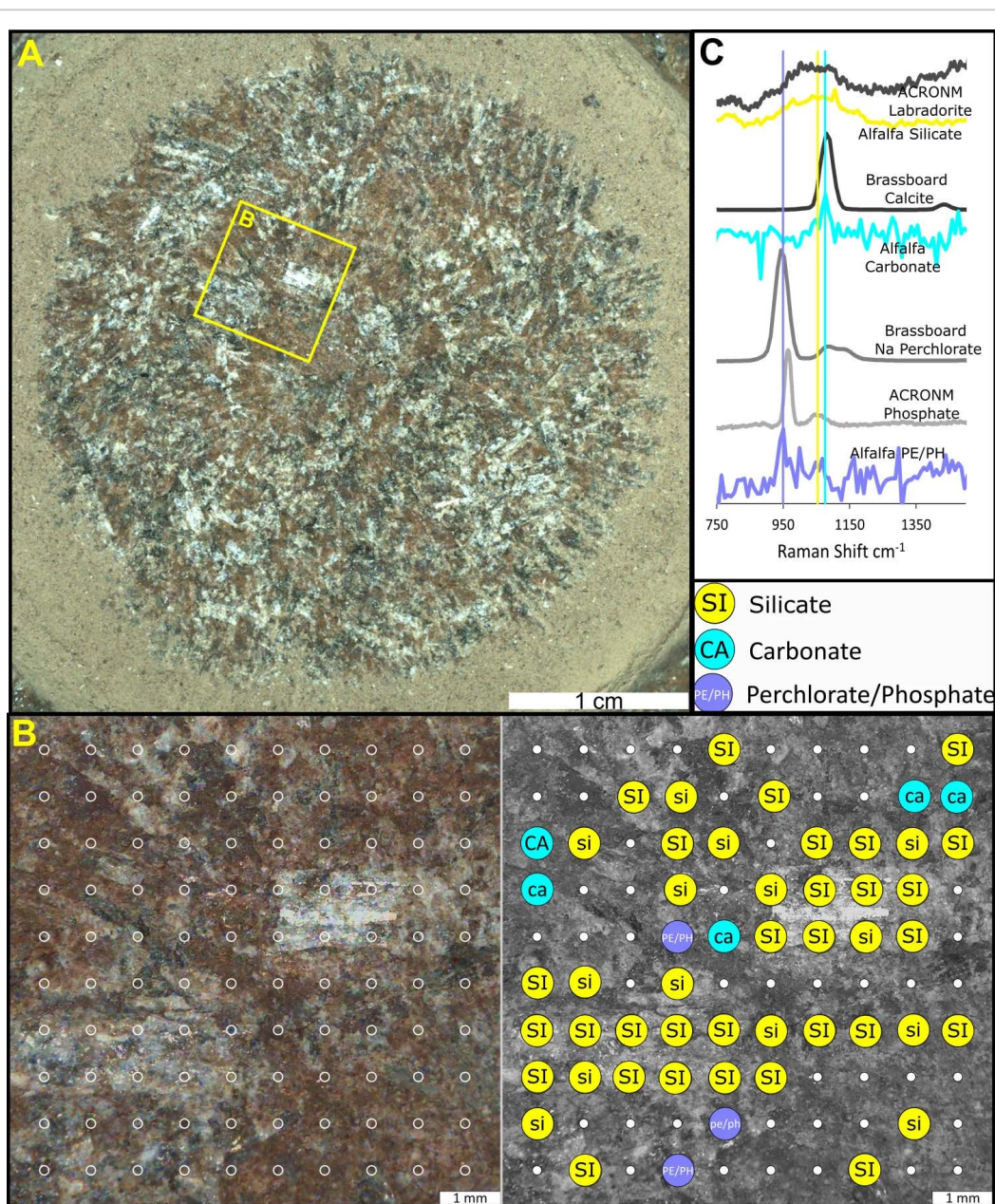


Figure 8. SHERLOC Raman mineral identifications from scan 0370_Alfalfa HDR_500_1 of target Alfalfa. A) The abrasion patch imaged by WATSON (image ID SIF_0367_0699544277_375FDR_N0110108SRCL08029_0000LMJ01). The yellow box indicates the location of the Alfalfa HDR scan. B) Colorized (left) and grayscale (right) ACI images (image ID SC3_0370_0699816293_742FDR_N0110108SRCL10600_0000LMJ01) of the region of the abrasion patch bounded by the yellow box in panel A. The white circles in panel B indicate the locations of SHERLOC analysis spots. Mineral identifications are indicated in the right panel. C) Representative Raman spectra from the abrasion patch of minerals, and mineral standard spectra collected on the SHERLOC Brassboard instrument at JPL and the ACRONM instrument at JSC. Vertical lines indicate peak centers. Spectra are offset along the y-axis for clarity.

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