CHARACTERIZING HYDRATION CARRIER PHASES IN ALTERED ROCKS OF JEZERO CRATER FAN AND FLOOR GEOLOGIC UNITS WITH SHERLOC ON MARS 2020

Introduction: The Mars 2020 Perseverance rover has explored fluvo-lacustrine sedimentary rocks within Jezero crater. Prior work showed that igneous crater floor Séítah and Máaz formations have mafic mineralogy with alteration phases that indicate multiple episodes of aqueous alteration [e.g., 1-4]. Building upon previous work [4] that studied hydration carriers in the igneous crater floor region, in this work [5], we extend the analyses of hydration to targets in the Jezero western fan delta, using the Scanning Habitable Environments with Raman and Luminescence for Organics and Chemicals (SHERLOC) instrument. We identified the alteration minerals present and determined the hydration states by comparison to terrestrial laboratory data. We then considered variability within and between targets, relating to the geologic units, to understand whether/how the fluid environments changed across time and space in the Jezero crater system.

Methods: SHERLOC targets: We analyzed the deep-UV Raman spectra of all stratigraphically in-place rock targets measured by SHERLOC at the Séítah and Máaz formations of the crater floor, the fan front (informally named the Shenandoah formation [6]), and the upper fan deposits of the sedimentary western fan.

Data analysis: We fit SHERLOC Raman spectra peaks with a 1D Gaussian profile using the SciPy library of Python. Prior to peak fitting, the median spectrum of the instrument flat field signal was subtracted to correct for instrument optics. Up to three Gaussian components with a constant baseline were used to model the 800-1200 cm\(^{-1}\) mineral region, where diagnostic peaks of minerals such as sulfate and carbonate are found. The 2800-3900 cm\(^{-1}\) hydration region was fitted separately with up to two Gaussian components and a linear baseline. The uncertainty of the peak position is estimated using Eq. (1) in [7].

The noise root mean square deviation (RMSD) was calculated from 2000-2100 cm\(^{-1}\), a spectrally quiet region. Fitted peaks of lower confidence (intensity < 2× noise RMSD) were filtered and removed in subsequent analyses. A second filter was applied to remove peaks with FWHM at the boundary of the applied constraints (20 < FWHM < 100 for the mineral region and 50 < FWHM < 300 for the hydration region).

Results: Sulfates and carbonates, separately or together, occur in targets across every geological unit.

Figure 1. Hydration peak position as a function of sulfate \(\nu_1\) peak position for various hydrous sulfates measured in the lab: (a) MgSO\(\cdot\)nH\(_2\)O, (b) CaSO\(\cdot\)nH\(_2\)O, (c) FeSO\(\cdot\)nH\(_2\)O and (Mg,Fe)SO\(\cdot\)nH\(_2\)O, (d) Fe\(_2\)(SO\_4)\(_3\)•nH\(_2\)O with values of n labeled in the plot. The area between the two sub-peak positions is shaded for clarity. "(am)" amorphous phase; "w" water per formula unit; "MH" and "LH": mid- and low-humidity polymorph of kieserite, respectively. (e) Hydration peak positions as a function of sulfate \(\nu_1\) peak position as measured by SHERLOC. The circles are numbered according to the four hydrated sulfate spectra types described in the text. The shaded regions in (a)-(d) have been reproduced in (e). [5]
Sulfates are a principal hydration carrier phase in all units, though the cations and/or hydration states of the sulfates and the cations of the carbonates vary across the units. The carbonates in the igneous crater floor appear to be more Fe-rich while those in the sedimentary western fan appear more Mg-rich.

From comparison of laboratory data to the hydration peaks in conjunction with sulfate peaks in the mineral region, we find negligible detections of highly hydrated sulfates (Fig. 1e). The sulfate symmetric stretch at ~1000 cm\(^{-1}\) coupled with a hydration peak at ~3400 cm\(^{-1}\) indicate that MgSO\(_4\cdot n\)H\(_2\)O (2 < \(n\) ≤ 5) is a likely hydration carrier phase in all units (cluster 1 in Fig. 1e). Low-hydration MgSO\(_4\cdot n\)H\(_2\)O (n = 1-2) is more prevalent in the fan (cluster 2 in Fig. 1e). Hydrated Ca-sulfates (>3500 cm\(^{-1}\) hydration peak; cluster 3 in Fig. 1e) matching bassanite are found only at the upper fan, while anhydrite is found in all units. We have not been able to definitively attribute hydration peaks at ~3200 cm\(^{-1}\) (cluster 4 in Fig. 1e), but a possibility is low-hydration amorphous Mg-sulfates (n ≤ 1).

Fig. 2 shows that there are three types of proportional relationships between the sulfate peak intensity and area of hydration band: (1) large increase in OH area with small increase in sulfate peak intensity observed for many crater floor and upper fan targets; (2) minimal increase in OH area with large increase in sulfate peak intensity, especially in Uganik Island, attributed to increasing anhydrite contribution to the spectra; (3) spectra with behavior in between (1) and (2) due to some contributions of anhydrite for Quartier, and bassanite that is more hydrated than anhydrite for Pilot Mountain.

**Discussion: Hydration states of sulfates in the present-day climate:** The persistence of the late-stage anhydrite and bassanite to the modern day implies arid conditions. While MgSO\(_4\cdot n\)H\(_2\)O (2 < \(n\) ≤ 5) identified at the crater floor and western fan is in equilibrium with present-day surface environmental conditions (≤3% RH and ~200-220 K during SHERLOC measurements), the occurrences in Jezero crater of Mg-sulfates with 1-2 waters, which are thermodynamically stable at temperatures above ~50°C, are out of equilibrium [9]. These low hydration Mg-sulfates could be stabilized by co-existing Ca-sulfates, which are also more frequently detected in the fan front than the crater floor or upper fan.

**Past environmental conditions:** Abundant anhydrous Ca-sulfate and fewer occurrences of hydrated Mg-sulfates in the stratigraphically higher fan front contrast with abundant hydrated Mg-sulfates and few anhydrous Ca-sulfates in the stratigraphically lower crater floor. These observations are consistent with a simple model for inflowing water where Ca-sulfates in the floor and fan are preferentially precipitated higher in the stratigraphy in the western fan due to their lower solubility, and the more soluble Mg-sulfates are precipitated at the stratigraphically lower crater floor due to evaporative concentration, similar to the process described by [8] for Gale crater Ca- and Mg-sulfates. Anhydrite and kieserite likely signify high ionic strength fluids rather than temperatures >50°C at the time of formation. The ionic strength of this fluid would likely have been lower in the stratigraphically higher upper fan, precipitating hydrated Ca-sulfate gypsum instead of anhydrite, and which subsequently dehydrated to bassanite. Later aqueous episodes may be responsible for the dissemination of Mg-sulfates within the sedimentary rocks in the fan. The carbonates in the upper fan also do not show clear textural associations, perhaps suggesting both alteration phases were deposited in the last stages of aqueous activity in the fan.

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