ANHYDRITE DETECTIONS BY RAMAN SPECTROSCOPY WITH SUPERCAM AT THE JEZERO DELTA, MARS.

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Introduction: The Perseverance rover landed in Jezero Crater, Mars, in February 2021, carrying several analytical instruments including the first Raman spectrometers to be ever employed in planetary exploration missions. The SHERLOC instrument [1] features an UV excitation source so it is mostly designed for the detection of organics and fluorescence, among other things. The SuperCam instrument [2, 3] is a multi-analytical instrument featuring several analytical techniques such as LIBS, Raman, visible and near-infrared (VISIR) reflectance, imaging and a microphone.

The SuperCam Raman technique uses a 532 nm pulsed excitation laser source with a 4 ns pulse, acquiring several (up to 400) shots per analyzed spot. The constraints imposed to space instrumentation make Raman spectroscopy on Mars challenging, needing to address a number of issues to improve the acquired signal at the acquisition level: optimizing the number of shots and on-chip accumulations -coadds-, dealing with fiber-induced Raman signals [4, 5] or post-processing noise and spikes. The SuperCam instrument has nevertheless been able to perform key mineralogical identifications with Raman spectroscopy during the first 640 sols of operations on Mars [6].

Previous sulfate detections on Mars: The Opportunity rover observed Ca- sulfate veins near Endeavor crater in Meridiani Planum [7]. The Curiosity rover identified abundant calcium sulfate veins throughout much of the Gale sedimentary strata using the LIBS spectrometer ChemCam [e.g., 8, 9], in combination with other experiments onboard such as the CheMin X-ray diffractometer [10]. The main challenge of the analysis performed by the ChemCam instrument was the identification of the hydration state of the analyzed samples. Though quantification of hydrogen with LIBS is challenging, as it strongly affected by matrix effects, the calcium sulfate veins detected with ChemCam were suggested to be bassanite [9, 11]. The APXS observations in Gale and Meridiani Planum had similar difficulty to quantify the hydration state. On the other hand, Raman spectroscopy, a technique never before used on planetary exploration missions, can easily differentiate between the hydration state of calcium sulfates [12].

Anhydrite detections by SuperCam Raman at the Jezero delta: The Perseverance rover is currently analyzing the sedimentary deposits at the delta front of the Jezero Crater Paleolake. Especially interesting are the regions called Hogwallow Flats and Yori Pass. These intervals are composed of sulfate- and phyllosilicate-bearing siltstones and sandstones [13] with recurrent presence of light-toned veins [14], see Fig. 1, including calcium sulfates.

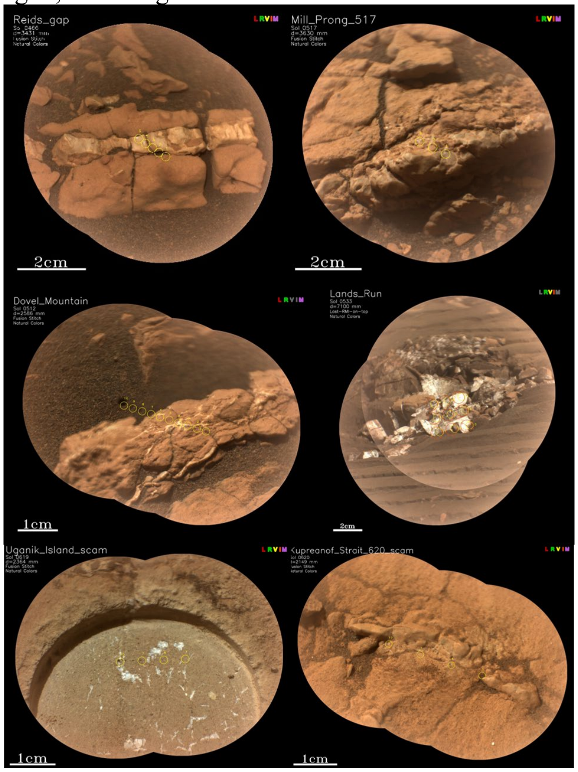

Fig. 1. Veins and patches analyzed with SuperCam

The improved capabilities of SuperCam to combine elemental observation with complementary molecular analysis (VISIR, but especially Raman), make this instrument specifically well-suited for mineral phase identification including hydration states of the samples, overcoming the limitations of previous experiments on Mars.

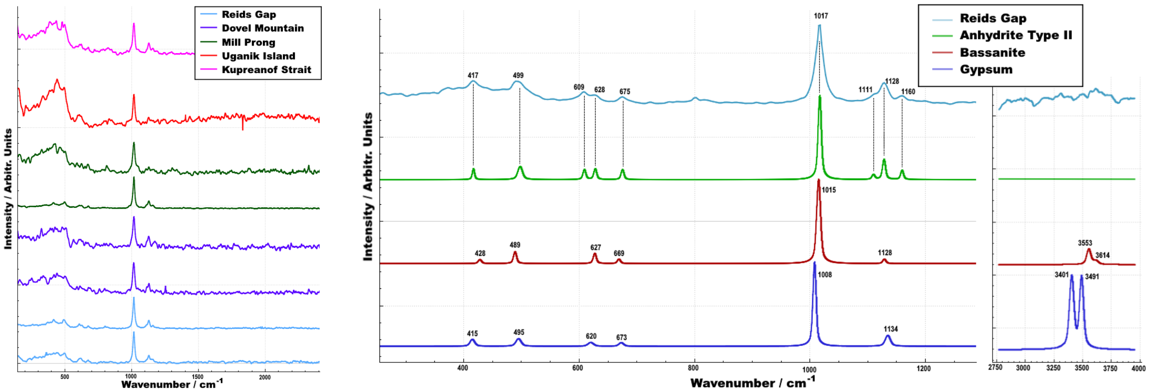

Figure 2. Raman spectra of anhydrite detections by SuperCam Raman up to sol 640, also showing the fiber bump response on the region around 500 cm^{-1}[4, 5] (left), and Ca-sulfate references compared to Reids Gap (right)

Indeed, the SuperCam Raman technique has been able to detect calcium sulfate in several targets, including Reids Gap (sol 466), Dovel Mountain (sol 512), Mill Prong (sol 517) and Lands Run (sol 533) at Hogwallow Flats, and Uganik Island (sol 619) and Kupreanof Strait (sol 620) at Yori Pass. The main advantage provided by Raman spectroscopy is that a clear discrimination between the three anhydrite polymorphs ($CaSO_4$), bassanite ($CaSO_4 \cdot 0.5H_2O$) and gypsum ($CaSO_4 \cdot 2H_2O$) is possible as long as their characteristic secondary peaks are detected [12]. As for the SuperCam Raman detections of Ca-sulfates, the identification of clear secondary Raman peaks at 609, 1111 and 1160 cm^{-1} unambiguously prove the detection of the anhydrite Type II (orthorhombic) polymorph. This interpretation has been further confirmed by the position of the main peak at 1017 cm^{-1} and by the lack of hydration features in the 3200-3700 cm^{-1} region [12]. See Fig. 2. The SuperCam LIBS spectra and subsequent H analysis is also consistent with anhydrite. However, VISIR shows evidence of hydration. Considering the unambiguous detection by Raman and the high sensitivity of IR to water bands, our current working hypothesis is that the ~1.4 µm and ~1.9 µm absorption bands observed in IRS spectra of Reids Gap are related to minor presence of OH and H_2O, either molecular in trace amounts or adsorbed on the sample surface.

Beyond anhydrite features, some of these Raman observations present a singular behavior related to an increased fast-decay continuum signal such as on Reids Gap or Lands Run. The nature of this signal is discussed in detail by Clave et al [15].

Conclusion: The SuperCam instrument provides a unique opportunity to combine different analytical techniques including Raman, LIBS and VISIR spectroscopies. This combination has proven to be very effective in the determination of the mineralogy of the Jezero Crater, being especially well-suited for the identification and characterization of light-toned materials and veins. In detail, the use of Raman spectroscopy has facilitated the correct identification – in combination with the other techniques- of the mineral phases at several locations during the Perseverance Crater Campaign (Na-perchlorate, olivines, feldspars, carbonates) [16-18]. In the delta campaign however, the Raman spectroscopy technique is so far showing an outstanding capability to complement the analysis by the other techniques in veins and light-toned materials.

Given the well acknowledged potential of Ca-sulfates for both habitability and organic preservation [19], the results summarized in this work highlight the key role that Raman spectroscopy plays in the refined characterization of light-toned veins, which has critical implications in the selection of the optimal targets to be fetched for the Mars sample return (MSR) mission.

Acknowledgments: We acknowledge the full SuperCam operations and science team. Spanish team partially funded by AEI Grants RED2018-102600-T, PID2019-107442RB-C31/AEI/10.13039/501100011033.

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