

**INTERPRETING THE CONTINUUM SIGNAL IN THE RAMAN SPECTRA ACQUIRED WITH SUPERCAM IN JEZERO CRATER, MARS.** E. Clavé<sup>1</sup> (elise.clave@u-bordeaux.fr), O. Beyssac<sup>2</sup>, G. Lopez-Reyes<sup>3</sup>, A. Ollila<sup>4</sup>, T. Fornaro<sup>5</sup>, P. Willis<sup>6</sup>, B. Bousquet<sup>1</sup>, S. Schröder<sup>7</sup>, K. Williford<sup>8</sup>, R.C. Wiens<sup>9</sup>, S. Maurice<sup>10</sup> & the SuperCam Team; <sup>1</sup>CELIA, Bordeaux, France; <sup>2</sup>IMPMC, Paris, France; <sup>3</sup>ERICA, Valladolid, Spain; <sup>4</sup>LANL, Los Alamos, New Mexico, USA; <sup>5</sup>INAF, Florence, Italy; <sup>6</sup>JPL, Pasadena, California, USA; <sup>7</sup>DLR-OS, Berlin, Germany; <sup>8</sup>BMSIS, Seattle, Washington, USA; <sup>9</sup>Purdue University, Lafayette, Indiana, USA; <sup>10</sup>IRAP, Toulouse, France.

### Introduction

On February 18<sup>th</sup>, 2021, the Perseverance rover landed in Jezero crater, Mars. Since then, its technical capabilities and scientific payload have been used to explore and characterize several geological units within the crater, identifying igneous formations on the floor of the crater [1] before investigating the sedimentary deposits at the front of the delta located to the West of the crater. Formed in a paleolake 3.5 to 4 billion years ago, the delta presents a variety of formations, some of which are considered to have high astrobiological potential [2-4].

The SuperCam instrument, onboard Perseverance, enables the characterization of geologic targets on the surface of Mars, at a distance of several meters around the rover [5,6]. A combination of spectroscopy techniques provides the elemental composition (LIBS) and mineralogy (VISIR and Raman) of the targets, while a remote micro-imager (RMI) provides context. In particular, SuperCam is one of first two instruments to perform Raman spectroscopy on Mars; using a 532-nm, 4-ns pulse laser excitation and time-resolution capabilities, SuperCam enables us to reject daylight entering the telescope and to observe either Raman scattering or luminescence excited in the rocks by the laser pulse. While remote Raman spectroscopy on the

surface of Mars is challenging, SuperCam Raman spectra have contributed to some key detections and characterization already [7-9].

Raman analyses of natural rocks in the laboratory – and especially when the field-of-view is millimetric as for SuperCam – often yield a strong continuum signal that may be due to different processes, including i) scattering in fine-grained material [6,10]; ii) luminescence, due to impurities or defects in mineral structures, sometimes related to irradiation [11,12]; iii) organic fluorescence [13]. Such continuum signals in SuperCam Raman data may therefore provide complementary information on the corresponding targets, if we can interpret its origin. We report observations of such continuum signal in Raman spectra acquired with SuperCam in Jezero crater; we characterize the corresponding targets and try to constrain the nature of this signal and its implications for Perseverance’s investigations.

**Identifying targets with continuum signal:** We analyze the Raman spectra acquired with SuperCam on Martian targets up to sol 640. Over this period, 490 spectra were acquired, on 44 targets. We applied an Independent Component Analysis (ICA, using the *FastICA* function of the *scikit learn* package in Python) to the set of Raman spectra restrained to the 170 – 1900

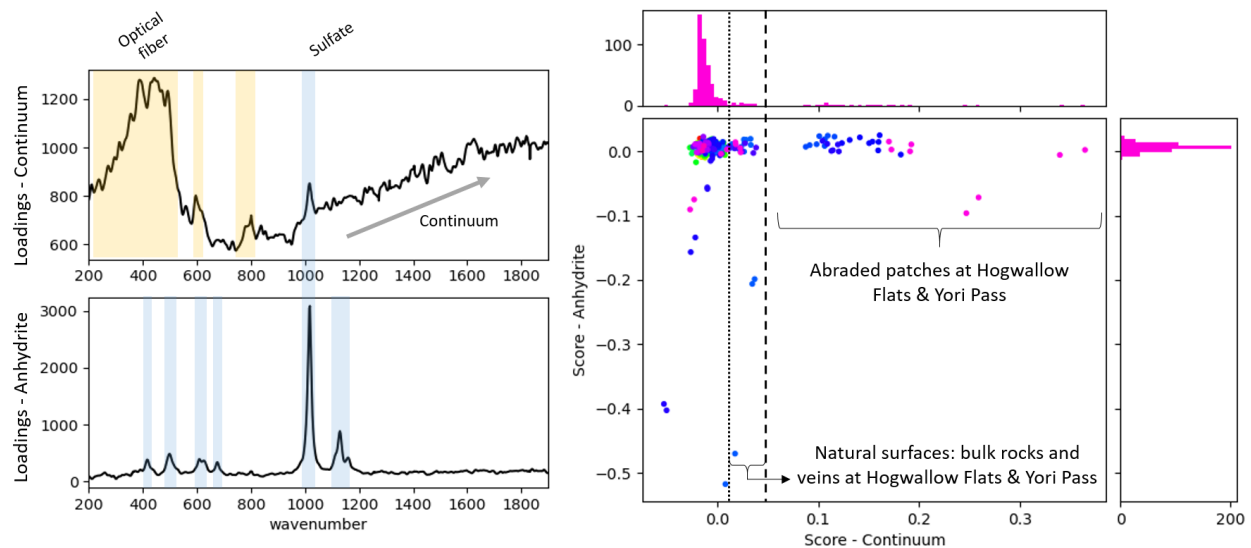


Figure 1 – Continuum and anhydrite components of a four-component ICA models : absolute value of the loadings on the left (the anhydrite component has a negative weight) and scores on the right, color-coded to the number of the sol the data was acquired on (green at the beginning of the mission; pink for latest data). The dotted and dashed lines in the scores plot correspond to our thresholds of 0.3 and 1 standard deviation, respectively.

cm<sup>-1</sup> range. In the resulting models, we identify one component corresponding to the Raman spectrum of anhydrite type II and another component with a significant continuum contribution (absolute value of the loadings shown in Figure 1). We use the scores of this continuum-bearing component to identify the targets presenting such continuum signal. Three targets (32 spectra) have ICA scores higher than 1 standard deviation (SD) of the scores distribution; four additional targets (24 spectra) have scores higher than 0.3 SD. These seven targets all belong to two specific geologic units in the delta front: Hogwallow Flats and its stratigraphic equivalent, Yori Pass [3,4]. These units contain Fe/Mg phyllosilicate- and sulfate-rich silt- to sandstones, with numerous Ca-sulfate veins, some of those characterized specifically as anhydrite [7,14]. These rocks are the finest-grained targets analyzed since the beginning of the mission; in particular, mean grain sizes were estimated around 50 micrometers for two of these targets based on SHERLOC ACI.

The highest ICA scores (above 1 SD) are achieved in the three abraded patches analyzed with SuperCam in these two units; the other targets (between 0.3 and 1 SD) correspond to bulk rocks and anhydrite veins analyzed without abrasion in both units.

Using SuperCam time resolution capabilities, we observed that the decay of the continuum is very fast: of the order of 10 ns or less, enabling to rule out many mineral luminescence centers to explain it [10].

### Discussion

Considering the fine-grained nature of the targets, it is possible that this signal may be due to light scattering at the grain interfaces, which would result in comparably short decay time. However, this process, although commonly observed in the laboratory, is still poorly understood and has not yet been characterized on Mars, since Raman spectroscopy has only been deployed on Mars so recently.

Since all of these targets present significant sulfate content, it is also possible that it may be due to some luminescence center in sulfates, either due to emitting centers like trace elements (e.g. REE) in the mineral structure, or possibly to radiation-induced defects. However, no exact match has been found yet for the signature observed with SuperCam in the literature, partly due to an imperfect correction of the instrument response function, that prevents from precisely localizing the maximum of emission.

Finally, we cannot rule out that the continuum signal observed in these seven Martian targets might be due to organic molecules in these rocks since a similar signal – with comparably short decay time – has been observed in organic-containing targets in the laboratory, and on Mars when analyzing the glue fixing the diamond

calibration target to the sample holder, or the ertalyte calibration target [15,16].

**Parallel with SHERLOC's data:** Three of the targets identified in this study were also analyzed with the SHERLOC instrument with deep UV Raman and fluorescence spectroscopy [17]. In these three targets, a fluorescence doublet was observed in the 300 – 330 nm range, which can be explained by either mineral luminescence – in particular Ce<sup>3+</sup> in sulfates – or the presence of organic molecules [18-20].

### Conclusion

Significant efforts are being deployed to constrain the origin of the continuum signal observed in some SuperCam Raman spectra. Detailed analysis of the Mars data acquired with the different scientific instruments onboard Perseverance is ongoing. In parallel, laboratory studies, as well as specific characterization activities performed on Mars are dedicated to better constraining the signatures resulting from the different processes considered here in fine-grained, sulfate-rich materials. Whether this signal is due to scattering in fine-grained materials, mineral luminescence or organic fluorescence, it can be used to identify, from a distance of several meters, targets with specific characteristics, including possibly targets with a high astrobiological potential.

**Acknowledgements:** We are grateful to the Mars2020 team for the continual effort that makes this extraordinary mission possible. This work has benefited from support from CNES and Région Nouvelle-Aquitaine.

**References:** [1] Farley et al., (2022) *Science*; [2] Farley et al., (2020) *SSR*; [3] Stack-Morgan et al., this conference; [4] Dehouck et al., this conference; [5] Maurice et al., (2021) *SSR*; [6] Wiens et al., (2021) *SSR*; [7] Lopez-Reyes et al., this conference; [8] Wiens et al., (2022) *Sci. Adv.*; [9] Clavé et al., (accepted) *JGR*; [10] Duy et al., (2017) *Anal. Chem.*; [11] Gaft et al., (2015); [12] Royer et al., this conference; [13] Fornaro et al., this conference; [14] Nachon et al., this conference; [15] Cousin et al., (2021) *SAB*; [16] Bernard et al., this conference; [17] Bhartia et al., (2021) *SSR*; [18] Sharma et al., in-review; [19] Shkolyar et al., (2021) *Icarus*; [20] Roppel et al., this conference.