IRON-SULFUR CONTAINING MINERAL PHASE IDENTIFIED IN JEZERO'S NORTHERN MARGIN UNIT WITH SUPERCAM LIBS DATA AND SPECTRAL UNMIXING. S. Schröder[1]*, E. Clavé[1], L. Mandon[2], P. Beck[2], O. Beyssac[3], P.B. Hansen[1,8], K. Rammelkamp[1], F. Seel[1], O. Forni[4], E. Dehouck[5], G. Foëx[6], T.S.J. Gabriel[7], P.-Y. Meslin[4], H.-W. Hübers[1,8], S. Maurice[4], S. Clegg[9], O. Gasnault[4], A. Cousin[4], R.C. Wiens[10]. [1]DLR-OS, Berlin, Germany. [2]IPAG, Grenoble, France. [3]IMPMC, Sorbonne Univ., Paris, France. [4]IRAP, Toulouse, France. [5]ENSL, Univ. Lyon 1, France. [6]Stenon, Potsdam, Germany. [7]USGS, Flagstaff, USA. [8]HU Berlin, Germany. [9]LANL, Los Alamos, USA. [10]Purdue Univ., West Lafayette, USA. (*Susanne.Schroeder[at]dlr.de).

Introduction: In February 2021, NASA's Perseverance rover landed on the floor of Jezero crater, initiating in-situ exploration and sample collection for future return to Earth. Jezero crater was selected for its high potential for past habitability, being linked to an ancient lake. After exploring the crater floor and the fan front to the west, the rover proceeded onto the fan and into the Margin Unit, a region where orbital data revealed particularly high carbonate signatures [1]. Perseverance also explored a crater rim-dissecting inlet channel, named Neretva Vallis [2], as well as several targets in terrain attributed to the Margin Unit in the north of Neretva Vallis.

The SuperCam LIBS (laser-induced breakdown spectroscopy) instrument is part of the rover's payload and collects data on the martian surface from remote distances of up to several meters. [3,4]. Sulfur is an element that is generally challenging to detect and quantify using LIBS but its emission features can be identified and quantified in targets with high sulfur content, such as Ca-sulfates and Mg-sulfates [5]. High sulfur in SuperCam LIBS data was observed at the delta front in several targets containing Ca-sulfates [6] (Fig. 1, left), which were identified as anhydrite using SuperCam Raman data [7]. At Bright Angel in Neretva Vallis, high sulfur was again seen together with high calcium, indicating again the presence of Ca-sulfates that was consistent with findings of other rover techniques. The sulfur emission lines in LIBS data are strongly superimposed by Fe lines and are particularly difficult to interpret in targets with significant iron content, complicating the analysis of mineral phases with both iron and sulfur. Spectral unmixing (SU) [8-10] provides a new and alternative way to analyze LIBS data to obtain semi-quantitative values for major and minor elements. In particular, sulfur scores can be obtained, unmixed from the contribution of iron in the spectra.

In this work, we present the results of SU applied to SuperCam LIBS data, reporting the detection of a mineral phase enriched in both sulfur and iron, with most detections occurring in a few targets in the northern part of the Margin Unit of Jezero crater's western fan.

Methodology Spectral Unmixing: The SU approach is a 'calibration-free' method that derives semi-quantitative elemental abundances exclusively from spectral data. This is complementary to the official quantification approaches by the team, which rely on the measurement of standards in the laboratory and regression models based on this data [11,12].

In SU, measured spectra are fitted by a linear combination of reference spectra that are computationally simulated for each element. To account for the complexity of LIBS data and its dependencies on experimental conditions, sample matrices, and ambient factors, multiple spectra for each element are simulated, varying plasma temperatures, electron densities, and concentrations, based on the Saha-Boltzmann equation and radiative transfer [8]. This is especially important for addressing the transient nature of LIBS data when applying SU to the time-integrated SuperCam data. Transition parameters are sourced from databases such as NIST and Stark-B, and the simulated spectral database is optimized by

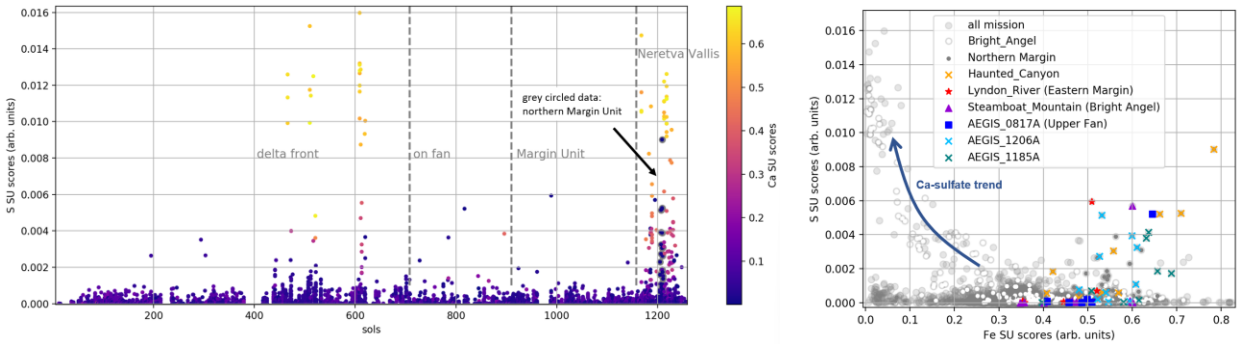

Figure 1: *(Left) The spectral unmixing scores of sulfur by sol # show local enhancements. After detecting Ca-sulfates at the delta front, more Ca-sulfates were seen at Bright Angel in Neretva Vallis after having left the Margin Unit. (Right:)Several sulfur enhancements were seen to correlate with enhanced iron content instead of with calcium.*

removing similar or linearly dependent spectra. SU "scores" are scalar values by which the simulated reference spectra are multiplied to match the measured LIBS data. Details on this methodology can be found in [3,4].

Results: Sulfur exhibits several emission lines, primarily in the range of 540–570 nm. Using the spectral unmixing approach, we found that Fe and S emission lines could be effectively separated and identified in SuperCam LIBS data. Several targets sampled a mineral phase enriched in both Fe and S, with most detections made in the northern part of the Margin Unit near the light-toned sedimentary Bright Angel site of Neretva Vallis [2], see Fig. 1 (right). Here, Ca-sulfates were also frequently detected, often associated with visible veins. The first target measured in the northern Margin Unit, with two out of ten positions enriched in Fe and S, was autonomously selected by the rover using the AEGIS software on sol 1185 (martian days since landing). AEGIS_1185A (Fig. 2, left) is a target with a major oxide composition [11] consistent with previous Margin Unit compositions, including two positions indicating the presence of carbonates [13]. AEGIS_1206A is another autonomously selected target, located in a small depression between the northern Margin Unit and Neretva Vallis (Fig. 2, middle; Fig. 3). Four out of ten positions showed enhanced Fe and S, and, as with AEGIS_1185A, these positions were not visually distinct from other areas on the targets. Haunted_Canyon is a bedrock target investigated using several LIBS rasters. A dark clast embedded in a brighter matrix was sampled, with most positions on the dark clast showing enhanced Fe and S emissions. Another position enhanced in Fe and S was seen in the raster of Hermit_Basin on the same rock. Single locations on some targets sampled before reaching the northern Margin Unit also exhibited combined Fe and S enrichments. Examples include one position on Lyndon_River in the eastern Margin Unit, one on Steamboat_Mountain at Bright Angel, and one on AEGIS_0817A, which was sampled on the upper fan.

Figure 3: *NavCam sol 1206 image showing the northern Margin Unit in proximity to the Neretva Vallis Bright Angel site where it was parked for this image.*

Discussion: While at Cheyava Falls at Bright Angel, contact science instrumentation PIXL found Fe-S occurences in so-called “poppy seeds” and “leopard-spots” [14] interpreted as sulfides that were there not seen by SuperCam, the Fe-S occurrence in the Steamboat_Mountain target seen by SuperCam less than a meter away suggests a similar nature. Since most SuperCam-detected Fe-S correlations are located in the northern Margin Unit outside of Neretva Vallis, this raises the question of whether the Fe-S mineral phase there shares the same origin as that at Bright Angel. Possible explanations, beyond sulfides, include Fe-sulfates indicative of local acidic fluids related to an igneous emplacement.

Conclusion: With SU, the contribution of superimposed Fe and S emission lines in LIBS data can be unmixed, providing an avenue for semi-quantified chemistry in challenging targets. With SU, we identified a mineral phase enhanced in Fe and S, mostly attributed to the northern Margin Unit and likely indicative of the presence of sulfides or Fe-sulfates.

References: [1] Horgan et al. Icarus 2020 [2] Mandon et al. this issue [3] Wiens et al. Space Sci. Rev. 2021 [4] Maurice et al. Space Sci. Rev. 2021 [5] Rapin et al. Nature Geosci. 2019 [6] Nachon et al. LPSC 2023 [7] Lopez-Reyes et al. LPSC 2023 [8] Hansen Dissertation 2022 [9] Schröder et al. LPSC 2023 [10] Schröder et al. LPSC 2024 [11] Anderson et al. Spectrochim. Acta B 2022 [12] Anderson et al. LPSC 2024 [13] Clavé et al. Mars conf. 2024. [14] Hurowitz et al. this meeting.

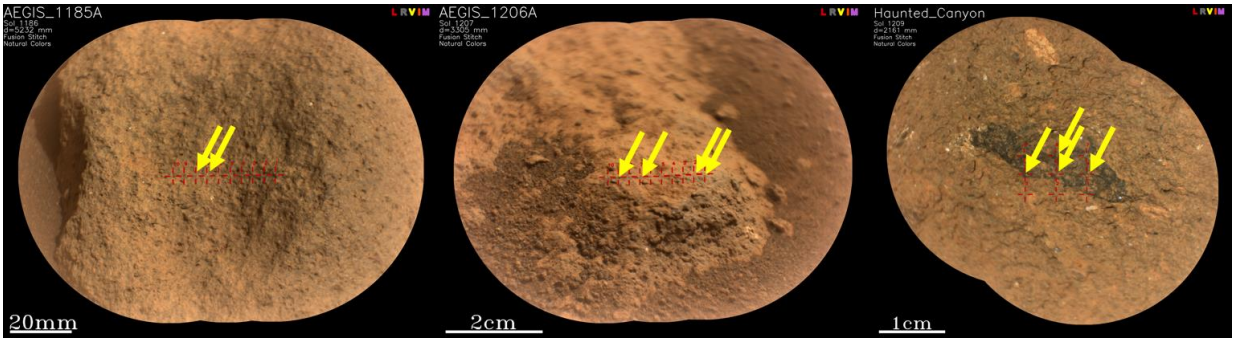

Figure 2: *Several targets with positions enriched in both sulfur and iron were observed in the northern Margin Unit (yellow arrows). On the target Haunted_Canyon, this enrichment was attributed to an embedded dark-toned clast.*