MINOR AND TRACE ELEMENT ENHANCEMENTS IDENTIFIED IN SUPERCAM LIBS DATA WITH SPECTRAL UNMIXING. S. Schröder[1]*, E. Clavé[1], P.B. Hansen[1,2], K. Rammelkamp[1], F. Seel[1], H.-W. Hübers[1,2], A. Cousin[3], O. Forni[3], O. Gasnault[3], P. Pilleri[3], E. Dehouck[4], P. Beck[5], O. Beyssac[6], G. Foëx[7], T. Gabriel[8], S. Maurice[3], R.C. Wiens[9]. [1]DLR-OS, Berlin, Germany. [2]HU Berlin, Germany. [3]IRAP, Toulouse, France. [4] ENSL, Univ. Lyon 1, France. [5] IPAG, Grenoble, France. [6]IMPMC, Sorbonne Univ., Paris, France. [7]Stenon, Potsdam, Germany. [7]IPAG, Grenoble, France. [8]USGS, Flagstaff, USA. [9]Purdue Univ., West Lafayette, USA. (*Susanne.Schroeder[at]dlr.de).

Introduction: With the SuperCam instrument onboard NASA's Perseverance rover, LIBS (laser-induced breakdown spectroscopy) data from Jezero crater is being obtained since the landing in February 2021 [1,2]. Spectral unmixing (SU) [3,4] provides a new and alternative way to analyze these data and to obtain semi-quantitative values for major and minor elements. We apply the spectal unmixing to all data along the traverse and track variations in inferred elemental composition. In particular, for minor and trace elements, SU provides interesting insights into the locally variating geochemistry and allows us to identify targets with remarkable enhancements.

In this work, we present some selected results of the SU applied to SuperCam LIBS data with a focus on minor element analysis such as the transition metals Ti, Cr, Mn, Ni, the two alkali earth metals Sr and Ba, and S and P as examples of nonmetallic elements.

Methodology Spectral Unmixing (SU): This approach is a 'calibration-free' approach and derives semi-quantitative elemental abundances exclusively from spectral data. This is in contrast 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 [5].

In SU, measured spectra are fitted using a linear combination of computationally simulated reference spectra for each element. To address the complexity of LIBS data and its dependencies on experiment parameters, sample matrix, and ambient conditions, multiple spectra for each element are simulated with varying plasma temperatures, electron densities, and concentrations based on the Saha-Boltzmann equation and radiative transfer. This is also particularly important to account for the transient nature of LIBS data in order to apply the SU to the time-integrated SuperCam data. Transition parameters are gathered from databases like NIST and Stark-B, and the simulated spectral database is refined by eliminating similar and linearly dependent spectra. Simple molecular features such as CaF are extracted from experimental data. The SU 'scores' are the scalar values by which the simulated elemental reference spectra are multiplied to fit the measured LIBS data. Details on the approach can be found in [3,4]. Elements exhibiting multiple emission features can be modeled with greater confidence compared to elements that display only one or a few emissions.

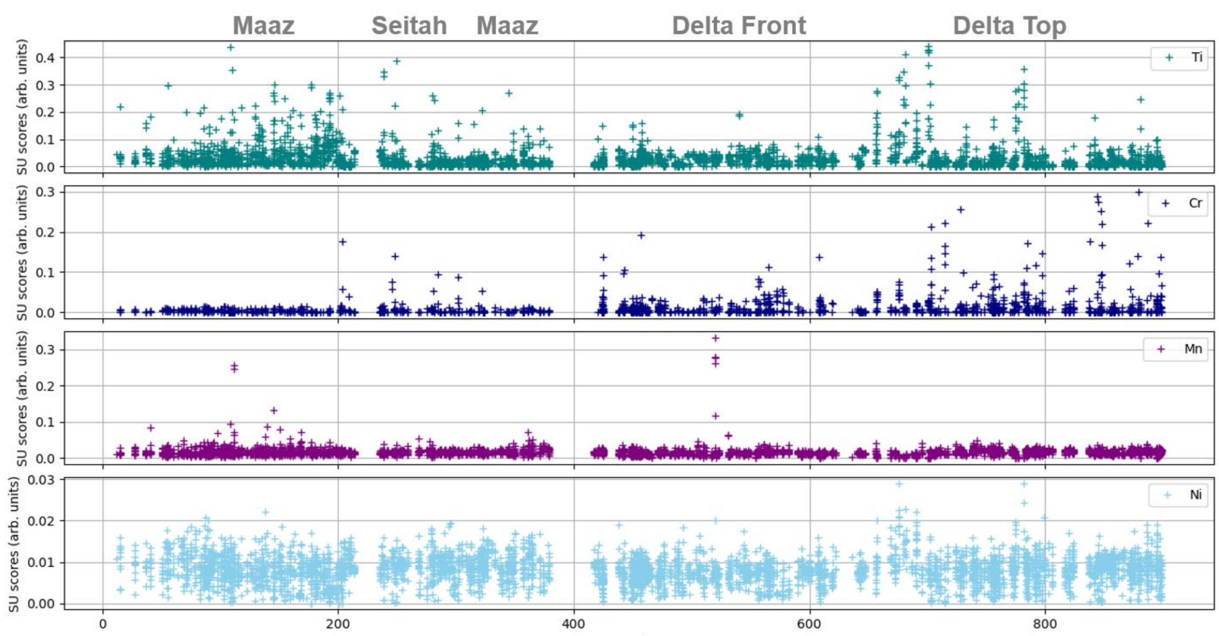

__Figure 1:__ The spectral unmixing scores of (from top to bottom) Ti, Cr, Mn, and Ni with sol. Local variations and enrichements can be seen. Every element varies on their own scale so that the scores cannot be directly transferred into concentrations.

Results - SU applied to SuperCam data: Due to the many emission lines of the transition metals, their scores are found very reliable for the detection of variations and identifying local enrichements. In Fig. 1, the scores of Ti, Cr, Mn, and Ni are plotted as a function of sol since beginning of the mission.

Ni enhancements are seen exclusively in Al and Ti enriched light-toned float rocks [6,7,8,9]. One example of these recently encountered light-toned float rocks with enhanced Al, Si and Ti as well as enhanced Ni scores is the target Elk_Mountain, see Fig. 2. This target, as some others of this group, interestingly also features an enhanced P score. Iron-nickel meteorites and respective very high Ni scores as seen in the ChemCam data obtained at Gale crater [10] are not present in the SuperCam data.

Recent Cr enrichments along the rover traverse can be attributed to the encountered olivine rich boulders in the upper fan and are interpreted to come from chromite or ulvöspinel [11] in these rocks of dunite-like composition while the pyroxene rich boulders do not show enhanced Cr scores [12]. These Cr enrichments as indicated by SU show deviations from our current regression models, as the latter is based on a pre-flight database of samples which do not extend to high Cr quantities.

Mn was seen only very unfrequently enhanced in individual targets with the most prominent example being the Hogback_Mountain [13] target that was sampled on sol 520 of the mission at the delta front and featured a dark coating (Fig. 3).

Similar to what was seen in ChemCam LIBS data, the SU scores proved well suited to identify Ca-sulfates through high Ca and S scores. The Ca-sulfates were encountered at the delta front [14] and were identified to be anhydrites by SuperCam's Raman spectrometer [15].

We are also currently investigating SU results for Ba and Sr (not shown) and results will be provided.

Conclusion: The SU yields scores through a moderate computational process, serving as semiquantitative values for various elements. Variations along the traverse can be seen and largely reflect those observed with other methods. We also observe local enhancements and unusual compositions in major and minor elements. A potential next step in our work may include the combination of SU with calibration data, a hybrid approach, which may help us to obtain real quantitative values from a regression.

References: [1] Wiens et al. Space Sci. Rev. 2021 [2] Maurice et al. Space Sci. Rev. 2021 [3] Hansen Dissertation 2022 [4] Schröder et al. LPSC 2023 [5] Anderson et al. Spectrochim. Acta B 2022 [6] Forni et al. this issue 2024 [7] Royer et al. AAAS subm. [8] Royer et al. this issue 2024 [9] Bedford et al. this issue 2024 [10] Schröder et al. this issue 2024 [11] Beyssac et al. this issue 2024 [12] Dehouck et al. this issue 2024 [13] Lanza et al. EPSC 2023 [14] Nachon et al. LPSC 2023 [15] Lopez-Reyes et al. LPSC 2023

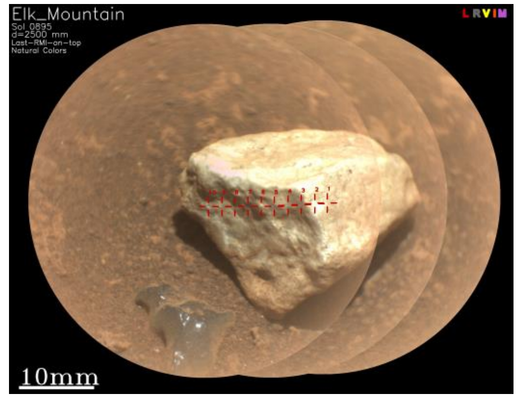

Figure 2: *Light-toned float rock sampled on sol 895 on the delta which next to enhanced Al, Si, and Ti also features enhanced Ni and P scores in most positions of the 10x1 raster.*

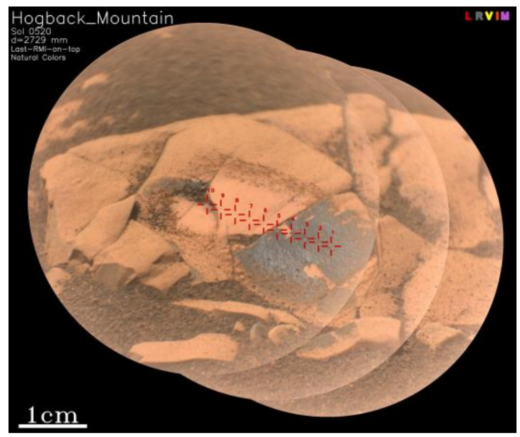

Figure 3: *The bedrock target Hogback_Mountain was analyzed with SuperCam on sol 520 at the delta front. Its high Mn scores from the dark-coated region are unique within the SuperCam data set.*

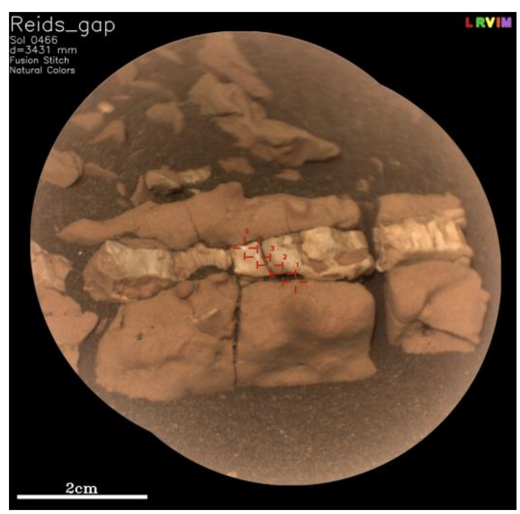

Figure 4: *Calcium-sulfate veins such as the target Reids_gap sampled on sol 466 at the delta front can be identified by their high S spectral unmixing score together with high Ca.*