INSIGHTS TO MINOR AND TRACE ELEMENT CONTENT IN CHEMCAM LIBS DATA WITH SPECTRAL UNMIXING. S. Schröder[1]*, K. Rammelkamp[1], P.B. Hansen[1,2], A. Cousin[3], O. Forni[3], O. Gasnault[3], P.-Y. Meslin[3], W. Rapin[3], E. Dehouck[4], P. Beck[5], J. Frydenvang[6], G. Foëx[7], S. Maurice[3], R.C. Wiens[8], H.-W. Hübers[1,2], N. Lanza[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]Uni Copenhagen, Denmark. [7]Stenon, Potsdam, Germany. [7]IPAG, Grenoble, France. [8]Purdue University, West Lafayette, USA. [9]LANL, Los Alamos, USA. (*Susanne.Schroeder[at]dlr.de).

Introduction: With the onboard ChemCam instrument, NASA's Curiosity rover has been acquiring ample of LIBS (laser-induced breakdown spectroscopy) data from Gale crater since the rover's landing in 2012 [1,2,3]. Spectral unmixing (SU) [4,5] provides a new and alternative way to analyze these data and to obtain semi-quantitative values for major and minor elements. In contrast to the official quantification approaches by the team [6,7,8], the SU method comes from the field of calibration-free LIBS and does not require comparison to standards measured in the laboratory. The SU approach is applied to all recent data and variations along the traverse are being tracked. In particular for minor and trace elements, the spectral unmixing provides interesting insights into the locally variating geochemistry and allows to identify targets with exceptional relative enhancements.

In this work, we present some selected results of the SU applied to ChemCam LIBS data with a focus on minor element analysis including the identification of iron-nickel meteorites and other unusual compositions.

Methodology Spectral Unmixing (SU): This approach, rooted in calibration-free LIBS, derives semi-quantitative elemental abundances exclusively from spectral data. 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 approach to time-integrated LIBS data such as from ChemCam. 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 are extracted from experimental data. The SU scores are the factors by which the simulated elemental reference spectra are multiplied to fit the measured data. Details on the approach can be found in [4,5].

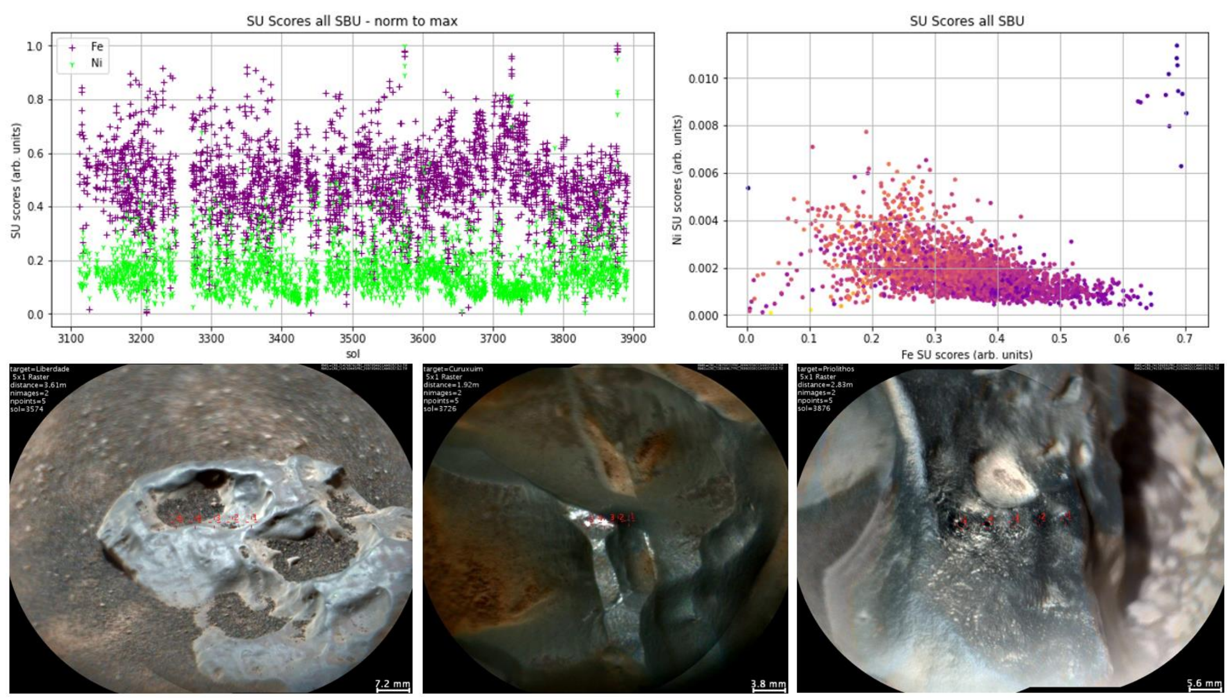

Figure 1: *(Top left) The SU scores of iron and nickel plotted as a function of sol on the sulfate bearing unit (SBU). The three sampled iron-nickel meteorites in that data set are easily identified by unusual high iron and nickel scores (top right). Below, the RMIs of the three meteorites informally named Liberdade, Curucuim and Priolithos are shown.*

Results - SU applied to ChemCam data: As reported previously [5], the SU scores proved well suited to identify calcium-sulfates, magnesium-sulfates, and sodium-chloride (halite) in the ChemCam LIBS data through enhanced sulfur and chloride scores, respectivly. New detections of these salts are continuously being identified in the lastest data.

As a first new example, the SU nickel and iron scores are shown as a function of sol for data obtained on the sulfur bearing unit (SBU) at Gale crater (Fig. 1, top right). When plotted against each other, the encountered and ChemCam sampled iron-nickel meteorites form a distinct group well separated from the rest of the data with highest scores in both elements. While these targets can of course also be identified with other approaches [9], the SU and in particular the derived nickel scores provide a suitable way to easily identify these samples in the LIBS data. The derived sulfur score adds to the analysis of the iron-nickel meteorites and was found particularly enhanced in the target Priolithos (Fig. 1, bottom right) while Liberadade and Curuxuim showed only low sulfur score levels.

Another target found with unusual minor elemental composition was Isla_Cangrejo sampled on sol 3572 at Contigo in the SBU which is a nodular bedrock on an erosion resistant cliff. All points of the 5x1 raster show enhancement in both manganese as well as chlorine. While the Mn and Cl scores are each only moderately enhanced and there are other targets with considerately higher Mn and Cl SU scores, respectively, the combination of enhancement in these two minor elements is unique in the extensive LIBS dataset of the SBU. Isla_Cangrejo also features high Na scores and sodium is likely the cation of the Cl salt, as halite detections are common in the region.

Other exceptional targets that can be indentified by the SU scores are the potential chondrite Gretna_Green [10] sampled with ChemCam on sol 2608 with enhanced Mg and Ni scores as well as the recently proposed Na-sulfates with enhanced Na and S scores [11].

Conclusion: The SU yields scores through a moderate computational process, serving as semiquantitative values for various elements. Particularly high values of a certain element can be identified as well as relations between different elements. Variations and local enhancements along the traverse can be seen and unusual compositions in major and minor elements can be identified. Despite originating in calibration-free LIBS, an interesting next step could be the combination with calibration data of the instruments and obtaining real quantitative values from a regression.

References: [1] Wiens et al. Space Sci. Rev. 2012 [2] Maurice] et al. Space Sci. Rev. 2012 [3] Maurice et al. J. Analytical Atomic Spec. 2016 [4] Hansen Dissertation 2022 [5] Schröder et al. LPSC 2023 [6] Clegg et al. Spectrochim. Acta B 2017 [7] Forni et al. Spectrochim. Acta B 2013 [8] Wiens et al. Spectrochim. Acta B 2013 [9] Meslin et al. LPSC 2019 [10] Lasue et al. LPSC 2020 [11] Hughes et al. this issue.

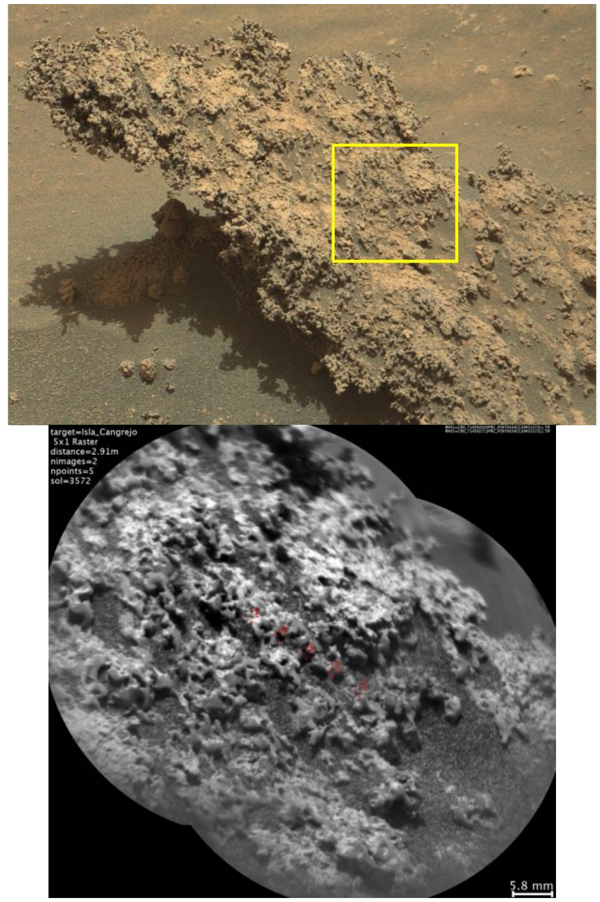

Figure 2: *The target Isla_Cangrejo was sampled by ChemCam with a 5x1 raster on sol 3572 of the MSL mission (top: mcam02633, bottom: RMI ccam01572).*

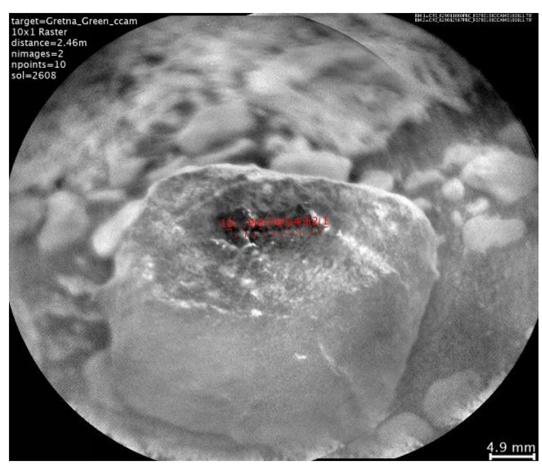

Figure 3: *The target Gretna_Green shows an exceptional combination of Mg and Ni enhancements and was previously suggested to be a chondrite [10].*