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► To cite this version:

S. Schröder, K. Rammelkamp, P.B. Hansen, F. Seel, A. Cousin, et al.. Semiquantitative analysis of chemcam and supercam libs data with spectral unmixing. 54th Lunar and Planetary Science Conference 2023, Lunar and Planetary Institute, Mar 2023, The Woodlands, Texas, United States. pp.2014. hal-04035451

HAL Id: hal-04035451

<https://hal.science/hal-04035451>

Submitted on 17 Mar 2023

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SEMIQUANTITATIVE ANALYSIS OF CHEMCAM AND SUPERCAM LIBS DATA WITH SPECTRAL UNMIXING. S. Schröder^{1*}, K. Rammelkamp¹, P.B. Hansen^{1,2}, F. Seel¹, A. Cousin³, O. Forni³, O. Gasnault³, P.-Y. Meslin³, P. Pilleri³, W. Rapin³, E. Clavé⁴, E. Dehouck⁵, O. Beyssac⁶, P. Beck⁷, S. Maurice³, R.C. Wiens⁸, H.-W. Hübers^{1,2}. ¹DLR-OS, Berlin, Germany. ²HU Berlin, Germany. ³IRAP, Toulouse, France. ⁴Univ. Bordeaux, France. ⁵ENSL, Univ. Lyon 1, France ⁶IMPMC, Sorbonne Univ., Paris, France. ⁷IPAG, Grenoble, France. ⁸Purdue University, Lafayette, USA. (*Susanne.Schroeder[at]dlr.de).

Introduction: The two NASA rovers Curiosity and Perseverance on Mars continue to acquire ample of LIBS (laser-induced breakdown spectroscopy) data from Gale and Jezero crater with the ChemCam[1,2,3] and SuperCam[4,5] instruments, respectively. Quantitative analysis, i.e. concentrations of the geological major elements (Si, Ti, Al, Fe, Mg, Ca, Na, K) are obtained from building calibration models based on measurements of known standards (several hundreds) in experimentally simulated martian atmospheric conditions in the laboratory with hardware close to the flight models[6,7]. These models rely on approaches from the field of multivariate data analysis, such as partial-least squares (PLS) regression or independent component analysis (ICA) regression[6,8] in the case of ChemCam and gradient boosting regression, PLS, random forest (RF), and LASSO in the case of SuperCam[7]. The derived major oxide compositions (MOCs) are provided by the teams. Minor and trace elements are quantified with univariate and multivariate approaches typically adapted to the element and sometimes also to the geochemical objective, e.g., [9, 10, 11, 12, 13, 14].

In this work, we present an approach for the calibration-free derivation of semi-quantitative values from the martian ChemCam and SuperCam LIBS data for major and many minor and trace elements.

Methodology Spectral Unmixing (SU): This approach comes from the field of calibration-free LIBS which means that all derived information such as elemental abundances are obtained solely on the basis of the spectral data. Measured spectra are fitted with a linear combination of reference spectra for every

element which were computationally simulated. In order to account for the complexity and many interdependencies of LIBS data on various parameters of the experiment but also the sample matrix and the ambient conditions, multiple spectra for each element were simulated with various temperatures, electron densities, and concentrations based on the Saha-Boltzmann equation and radiative transfer [15]. 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 and SuperCam. The transition parameters were carefully collected from public data bases such as NIST and Stark-B and partially extrapolated and estimated if not available. The spectral data base was then reduced, removing spectra of high similarity and those that can be obtained by linear combinations of other spectra. Simple molecular features were obtained from experimental data.

The measured LIBS data for SU analysis needs to be calibrated, i.e. corrected for the instrument response, so that the emission lines feature intensity ratios following the Saha-Boltzmann equation. All spectra are normalized to total emission intensity. The background is fitted by a superposition of broad Gaussians. We apply the SU here only to LIBS data averaged over the last 25 of the typically 30 acquired single-shot spectra per position. The SU scores are the factors by which the simulated elemental reference spectra are multiplied to fit the measured LIBS data. Elements with multiple emission features in the spectral data base can be modeled with higher confidence than elements with only single or few emissions.

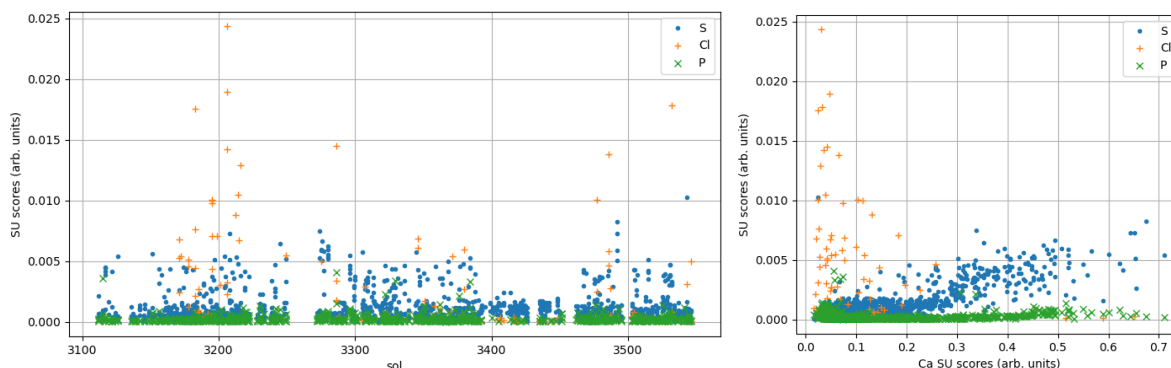


Figure 1: (Left) The SU scores of sulfur, chlorine and phosphorous derived from ChemCam data are shown for the sols 3110 to 3547 when the rover started to explore the basal sulfate bearing unit. The trend of the Ca SU scores and the S SU scores indicates the detection of calcium sulfates (right).

The following elements and features of simple molecules are typically found in LIBS data of geological samples: Al, Ba, C, Ca, Cl, Cr, Fe, H, K, Li, Mg, Mn, Na, Ni, O, P, Rb, S, Si, Sr, Ti, CaO, CaF, CaCl, C₂. Though present in the modeled spectral data base, too, for the following elements scores equal to zero were obtained, meaning that their scores were under a certain threshold value and therefore not relevant: Ag, Ar, Au, B, Be, Br, Cd, Ce, Co, Cs, Cu, Dy, F, Ga, Ge, Hg, I, In, Ir, La, Mo, N, Nb, Nd, Pb, Sc, Sn, V, W, Y, Zn, Zr. It will be investigated if the approach can be tuned to find elements such as Br, Cu, Ge, and Zn.

Results - SU applied to ChemCam data: The SU approach was applied to data obtained with the ChemCam instrument between sols 2160 and 3547. For ChemCam, csv format of the clean calibrated spectra (CCS) are used.

As an example, scores of sulfur, chlorine, and phosphorous in recent ChemCam data obtained on the basal sulfur unit are shown with the sol on which the data was obtained (Fig. 1, left). A trend of the Ca SU score with the S SU score can be seen, indicating the sampling of calcium sulfates (Fig. 1, right). A less steep trend can be seen between the Mg and S SU scores (not shown here), pointing to the detection of magnesium sulfates, too. The Cl SU scores show a clear trend with Na SU scores, with only moderate SU scores of oxygen (see color coding of Fig. 2) indicating the presence of halite and not perchlorates.

When looking at data acquired earlier in the mission, also other reported findings can be seen from this alternative approach. For example the SU scores of Mn show nicely the locally elevated abundances around the Mary Anning and Groken drill sites [e.g., 16].

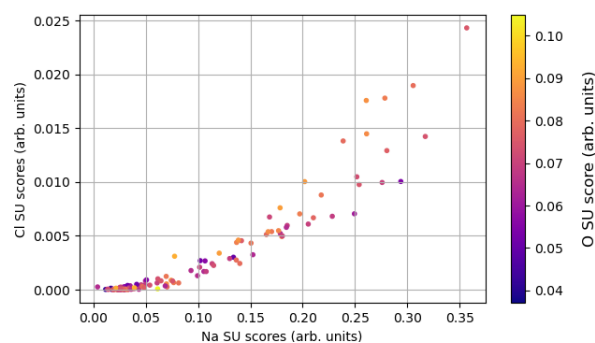


Figure 2: SU scores of Cl as a function of the SU scores of Na and color-coded by the SU scores of oxygen, suggesting the presence of halite (ChemCam sols 3110-3547).

Carbon is a particularly challenging element to quantify in martian LIBS data, since carbon from the martian atmosphere always contributes to the plasma and its emission. With the SU approach, a carbon score

can be obtained. Once the dependence of the distance to the target is taken into account, similar to what can be seen in [17], the carbon score shows seasonal variations.

Results - SU applied to SuperCam data: The SU was applied to data acquired up until sol 538. For SuperCam, calibrated data record (CDR) LIBS data were used in the provided FITS format.

A first application here was the study of the carbon and oxygen scores for the search of carbonates in the data and comparing to the results presented in [18]. Here, too, dependencies on the distance need to be taken into account before interpretation of high C score targets. In the LIBS data obtained at the delta, the highest C SU scores were seen to date. The carbon/oxygen SU analysis proved also particularly useful for the identification of outliers in the martian data such as from suboptimal focus on targets with very rough surfaces.

Also, in the SuperCam data, the detection of calcium sulfates can be seen from a clear trend of the Ca SU score and the S SU score. Additionally, a trend of Sr with S is observed for some targets. The SU approach allows further to identify targets with elevated P and Cl in the SuperCam data. It is also in line with other findings reported by the SuperCam team, for major as well as for minor elements, such as the detection of targets with elevated Mn or Cr and, for example, correlations of high Cr mostly with elevated Fe [e.g., 19]. Variations of Ba, Li, Ni, Rb, and Sr along the traverses can also well be seen in the SU scores.

Conclusion: The scores from the SU are obtained with moderate computational effort and can be used as semi-quantitative values for various elements. Particularly high values of a certain element can be identified as well as relations between different elements. Variations along the traverse can be seen and in the case of carbon mostly contributed by the martian atmosphere a dependency on the local season is observed. The results that can be obtained with the SU scores are in line with the quantitative values and findings officially provided by the ChemCam and SuperCam teams.

Although the SU approach comes from the field of 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.

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