

FROM UNIVARIATE ANALYSES OF THE ONBOARD CHEMCAM CALIBRATION TARGETS TO ESTIMATES OF MARTIAN ROCK AND SOIL COMPOSITIONS

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Introduction: The Curiosity rover carries body-mounted calibration targets that have been specially designed for the ChemCam instrument ([1], [2]). These samples have been analysed periodically during the first 90 sols in order to control i) the stability of the spectrometers (possible shift in wavelength sol to sol or depending on the spectrometer temperature) and ii) to obtain good statistics on the target compositions. There are two overall methods for determining elemental compositions from the ChemCam spectral data. One method uses multivariate techniques, specifically partial least squares (PLS), to interpolate compositions from a set of ~60 standards analyzed by ChemCam prior to launch [3]. The PLS results have been used to provide rapid preliminary compositions on the tactical timeline, and rely on the onboard calibration targets for sanity checks. Another method, described here, uses the onboard targets to infer element ratios by ratioing relative peak areas. As discussed extensively in the LIBS literature, each method can have advantages and disadvantages. PLS can overcome chemical matrix effects ([4], [5]) but is subject to the appropriate coverage of the training set. On the other hand, the univariate analyses are simpler to implement. This paper presents the potential of using these onboard ChemCam calibration targets (CCCT) to assess martian rock and soil compositions using univariate analysis.

ChemCam Calibration Targets: The compositions of the silicate targets have been chosen to simulate expected rocks on the Mars surface, with typical compositions observed as picritic, basaltic shergottite and norite basalts. A natural obsidian glass from Macusani, Peru has been added for high Silica and low Iron contents. Four sulfate-bearing samples complete the set of geological reference samples. Two other CCCTs, graphite and titanium, were not used in this study. All of the silicate samples, natural or synthetic, are highly homogeneous with a RSD lower than 10% for concentrations higher than 0.01 oxide weight % [1]. Ceramic targets are characterized in Vaniman et al. [2] and they are intended to mimic the compositions of Mars sedimentary rocks or soils with low to high sulfate contents. Suitable homogeneity was hard to obtain during their production due to the difficulty of retaining and quenching different phases (e.g. sulphates); however they are essential for ChemCam calibration.

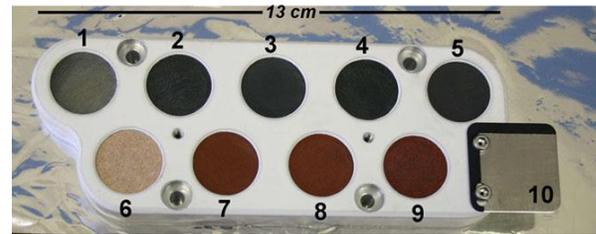


Figure 1: Onboard CCCT, 1-Macusanite, 2-4 silicate targets, 5-Graphite, 6-9 ceramic targets and 10-Titanium plate (from [3])

Methodology: The ChemCam instrument allows acquisition of LIBS emission spectra on three spectrometers, and each element can be characterized by one or various emission lines. We have selected the most stable emission lines for major and some trace elements in order to use the emission areas of the peaks after normalization to the total emission of each spectrum. It can be noticed that emission is more efficient in the ceramic samples than in the silicate targets, due to a better laser coupling for the ceramics. The LIBS spectra presented here averages of 30 LIBS shots on each observation point. We have used different sets of CCCT analyses done during sols 27, 49, 76 and 112, to obtain good statistics. The selected emission lines are the following: Na 589 and 818nm, Ca 318 and 422nm, Si 288 and 390nm, K 766 and 770nm, Mg 285 and 448nm, Al 309 and Fe 438 and 404 nm.

Results for direct element: A first approach is to compare emission peak areas versus the known compositions of the CCCT for all of the major elements. Figures 2 and 3 present calibration curves obtained for Mg and Fe respectively. As each CCCT has been analysed several times, several points are reported for each set of analyses. Thus, the homogeneity or the heterogeneity of the CCCT is observed on the plot: the results of homogeneous targets cluster tightly (i.e. norite, picrite, with a relative standard deviation less than 10%), but scattered points are typical of heterogeneous targets as seen for the medium-sulfur ceramic target (MEDS) for Fe content (Fig.3). However, calibration curves present fairly good correlation coefficients, even for those with the highest heterogeneity in the CCCT. Thus, for each element peak area it is possible to obtain an estimate of the elemental content for each LIBS analysis.

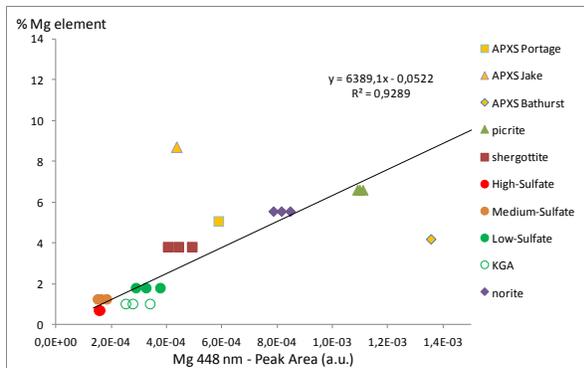


Figure 2: Univariate estimates of the Magnesium using the 448 nm emission line. Three inter-comparisons with APXS results obtained on martian rocks and soils are also shown. HIS, MEDS, LOS, and KGA refer to high, medium, and low-sulfur nontronite and kaolinite ceramics.

To test this univariate approach, three APXS MSL analyses were also plotted. This cross-calibration provides a comparison of our estimates to external analyses obtained on the same targets (i.e., APXS vs. LIBS). Jake Matijevik [6] and Bathurst [7] are martian rocks and Portage is a martian soil. As Jake Matijevik is heterogeneous in grain size and composition [4] at the spatial scale of the ChemCam beam (~0.4 mm dia.), the univariate estimates are not always in agreement with APXS data, especially for the iron and magnesium direct element estimates. However, the finest grained Portage soil shows good agreement for iron as well as for magnesium. Bathurst shows very similar Fe compositions from ChemCam and APXS analyses (average values, Fig. 3).

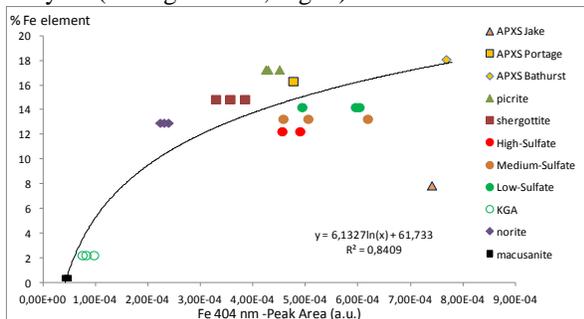


Figure 3: Univariate estimates of iron using the 404 nm emission line. Three APXS mean analyses obtained on martian rocks and soils are also reported for comparison.

Results for specific element ratios: Geologists usually use element ratios to compare with reference minerals or to compare with previous martian compositions. This element ratio approach is also classically used by the LIBS community because of differences in overall signal intensity between samples. For the examples of Al/Si and Mg/Fe+Mg (so-called

#Mg number), the calibration curves (Fig. 4 and Fig. 5) present better correlation coefficients than those obtained for direct peak area/abundance estimates (not shown here). The APXS data for rocks and soils are in good agreement with our univariate estimates, as they plot along our calibration line. The ChemCam and APXS data agree very well for Portage soil, which is fine grained.

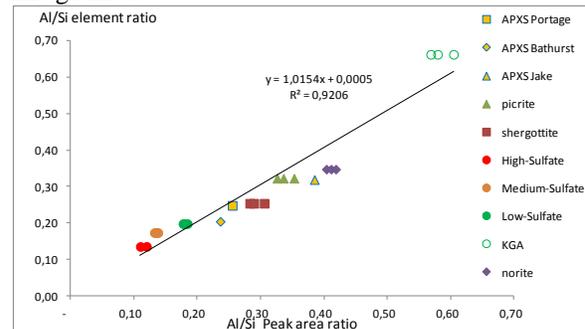


Figure 4: Univariate estimates of Al/Si ratios using the 309 nm Al emission line and 288 nm Si emission line.

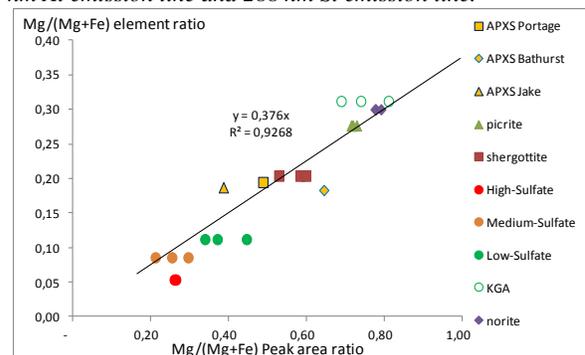


Figure 5: Univariate estimates of Mg/(Mg+Fe) ratios using the 448nm Mg emission line and 438 nm Fe emission line.

Conclusions: Using three sets of CCCT analyses, we are able to obtain univariate calibration curves that permit determination of element contents or elemental ratios. Comparison to APXS data is very constructive, as our univariate results are generally in good agreement, even if the analysis spots are very different in scale. To improve the coefficient of correlation of the calibration curves, we must acquire more LIBS analyses of the CCCT, to better constrain statistics. Thus, univariate analysis can be used for some elements when ChemCam analysis is completed on martian targets, to rapidly acquire first estimates of oxide weight percentages, as already demonstrated with the PLS technique [6].

References: [1] Fabre, C. et al. (2011), *Spectrochimica Acta*, 66, 280-289, [2] Vaniman D. et al. (2012) *SSR*, DOI 10.1007/s11214-012-9886-0, [3] Wiens, R.C. et al. (2012) *SSR*, DOI 10.1007/s11214-012-9902-4, [4] Lasue, J. et al. (2013), [5] Clegg, S. et al. (2013), [6] Cousin, A. et al. (2013), [7] Sautter, V. et al. (2013), [8] Forni, O. et al. (2013), this meeting.