LIBS CHARACTERIZATION OF MARTIAN SOIL ANALOGS: IMPLICATIONS FOR THE CHEMCAM ANALYSES OF AEOLIAN SEDIMENTS AT GALE CRATER. G. David[1], P-Y. Meslin[1], E. Dehouck[1,2], G. Berger[1], A. Cousin[1], O. Forni[1], J. Lasue[1], O. Gasnault[1], R. C. Wiens[3], S. Maurice[1], W. Rapin[4], J.F. Fronton[5]. [1]Institut de Recherches en Astrophysique et Planétologie, Toulouse, France, [2] LGL-TPE, Lyon, France, [3]LANL, Los Alamos, USA, [4]DGPS-CIT, Pasadena, USA, [5]CNES, Toulouse, France ; [gael.david@irap.omp.eu]

Introduction: The Curiosity rover has been investigating Mars' surface at Gale Crater since 2012. Its payload enables the analysis of the soil composition, which is especially interesting because it mixes local and regional components, and is thought to be generally representative of martian average crust composition [1]. Constraining the nature and composition of alteration phases in martian soils is also important because they are direct clues to recent and past environmental conditions of the planet. The CheMin (Chemistry and Mineralogy) X-ray diffractometer showed that soils at Gale contain a significant amorphous component, about 35 (± 15) wt% [2]. Mass balance calculations using the CheMin mineralogy and the bulk chemical composition measured by the Alpha particle X-ray Spectrometer (APXS) suggest that this amorphous component is lightly enriched in Fe and is Si-poor [3]. The water released during heating of sieved soil materials by SAM (Sample Analysis at Mars [4]) could be associated to the amorphous component because CheMin did not detect any hydrated minerals. A better understanding of the composition of this non-crystalline component as well as its origin, which are still poorly constrained, are important to our understanding of the alteration processes that prevailed at the surface of Mars.The Laser Induced Breakdown Spectroscopy (LIBS) method on the ChemCam (Chemistry and Camera) instrument [5,6] is well suited to directly probe the amorphous component. It is the first Mars surface instrument to provide characterization of elemental chemistry at a submillimeter scale. However, soils contain a large diversity of grains, whose size can be smaller and/or larger than the 350-550 μm of the laser sampling area. The primary aim of this study is to better constrain the grains' size effect on the LIBS signal. We also want to explore the possibility to extract information from the ChemCam dataset on the physical state of the amorphous component, which can be useful to determine its origin. Two endmember hypotheses were explored: (1) the amorphous component can be present as a mechanical mixture in the soil with the crystalline component, or (2) it can form an alteration rind or a surface coating on the grains, due to precipitation from a solution or to the presence of a dust cover.

Method: We produced in the laboratory simple mixtures representing our two hypotheses. Mechanical mixtures were obtained by mixing unaltered basaltic grains (JSC-1 lunar simulant [7]) and altered basaltic grains (JSC-1 martian simulant [8]), with different ratios and sieved grain sizes. Grains with surface coatings were simulated by precipitating magnesium sulfate ($MgSO_4$) from a saturated solution onto basaltic grains of JSC-1 lunar simulant, with different grain sizes and different concentrations of sulfate. LIBS analyses were performed with the ChemCam testbed available at IRAP in Toulouse. Samples were placed in a martian chamber reproducing the pressure (~7mbar) and atmospheric composition (mostly CO_2, plus 1.6 % Ar and 2.7% N_2), in which the flight model operates. Each sample was probed on 5 locations with 30 laser shots. The spectra obtained have been processed in the same way as the ChemCam data from Mars, except for the instrument response function [5]. A multivariate Independent Component Analysis (ICA) was used as a qualitative method to compare spectra [9]. The ICA gives a correlation factor between unknown spectra and 10 independent components corresponding to elements Si, Ti, Al, Fe, Mg, Ca, Na, K, H and Li. This method allows the observation of chemical variations that can be interpreted as mineralogical changes.

Results: In mechanical mixtures, this study shows a linear relationship between the ICA scores of Fe, Si Na, H and the concentrations of the alteration products, as seen in Fig. 1. This relationship seems to be independent of grain size. The hydrogen ICA scores have the same behavior as for other elements, which demonstrates that hydrogen signal in soils is not strongly affected by the roughness effect [10], which affects to some extent its application in rocks. Therefore, hydrogen can be used confidently as a geochemical marker to constrain the nature of hydrated minerals present in martian soil, and particularly the chemistry of the amorphous component.

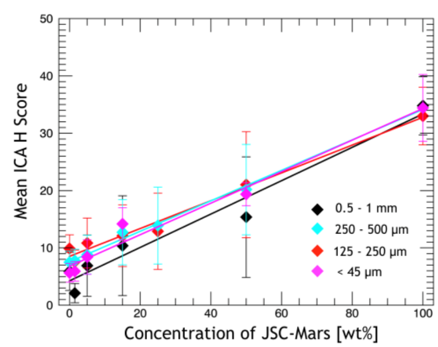

Figure 1: Hydrogen ICA scores for mechanical mixtures between JSC-1 lunar simulant and JSC-1 martian simulant for 4 ranges of grain sizes. Error bars represent the standard deviation.

Regarding the effect of grain size, the scatter in the ICA scores shows that, in mechanical mixtures, the chemical end-members start being directly probed for sizes equal to or greater than 125-250 μm. Indeed, a mixing line between the end-members can be observed (Fig. 2.a). However, their exact chemistry cannot be directly obtained for grain sizes lower than 125 μm because the data cloud does not reach the end-member groups (in red and blacks, Fig. 2.b).

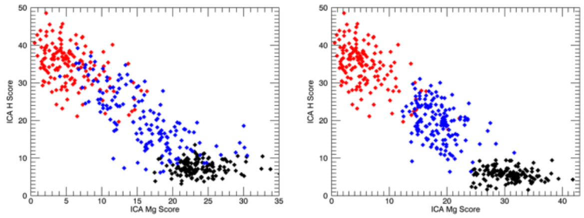

Figure 2: ICA Mg scores as a function of ICA H scores for pure JSC-1 lunar simulant (black dots), pure JSC-1 martian simulant (red dots) and two mechanical mixtures of these products (50 wt% of alteration compound) with grain sizes: 125-250 μm (left) and < 45 μm (right).

For fine-grains (< 500 μm) with a surface coating, the ICA scores are almost totally dominated by the surface chemistry (Fig. 3). This result shows that for martian applications, measurements of unconsolidated sediments, ChemCam can be strongly affected by the presence of coating due to the low penetration depth of laser shot (estimated to be about 1 μm in rocks), combined with the movement of grains due to the plasma shock wave refreshing the analyzed surface after every shot.

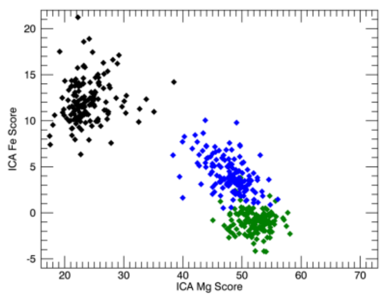

Figure 3: ICA Mg scores as a function of ICA Fe scores for pure JSC-1 lunar simulant grains 125-250 μm (black dots), pure magnesium sulfate (green dots) and grains JSC-1 lunar simulant grains (125-250 μm) with 15 wt% $MgSO_4$ surface coatings (blue dots).

This study also highlights a signature that allows us to make a distinction between the two kinds of mixtures for coarser grains (> 500 μm). Indeed a monotonic variation of ICA scores with the shot number can be noticed for grains carrying a surface coating. This signature requires that grains and coatings have distinct chemical compositions. This monotonic variation, which is absent for mechanical mixtures, can be interpreted as a gradual ablation of the grain coating first and then of the basaltic grain itself. Coatings thickness are checked with a microscope, which enable to estimate the ChemCam ablation ability between 0.3 μm and 1.5 μm per shot in soil.

Discussion: These laboratory observations allow a better understanding of the martian dataset. We demonstrate the possibility to retrieve information on the physical state of soil components in a direct (compositional variation with shot number) or indirect way. Indeed, grain sizes combined with ICA scattering can bring additional information onto the physical structure of the soil's grains. A direct application can be made to the analysis of the aeolian deposits of the Bagnold Dunes [2], where ChemCam analyses were done on different sieved sections: on grains smaller than 150 μm and grains between 150 and 500 μm. The result (Fig. 4.) shows the ICA Na and Al scores of these two size fractions, and at least two end-members can be noticed. Analogous to our laboratory data, the increase of grain sizes (red cluster to blue cluster) leads to an increased scattering in the mains correlation directions. According to laboratory experiments, this can only happen if the two components are present in a mechanical mixture rather than grains with surface coatings. Indeed, we demonstrated that for grain coating, the chemistry is equivalent for all the shots (in the <150 and 150-500 μm size ranges) because LIBS only probes the very superficial grain parts and their expulsion constantly refreshes the surficial material between shots. The result makes sense geologically because the two end-members of figure 4 are the mafic and felsic components detected by CheMin [11], and they are most likely mechanically mixed. This Mars observation enables us to confirm the ICA score behaviors in mechanical mixtures.

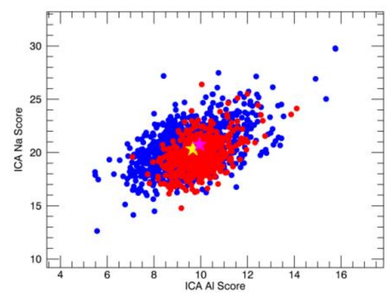

Figure 4: ICA Na and Al scores of Bagnold Dunes for grains lower than 150 μm (red dots; mean : yellow star), and between 150-500 μm (blue dots ; mean : pink star).

Conclusion: This work shows that LIBS can determine the physical state of a granular medium as well as information on the chemistry of coatings. Further ChemCam analyses need to be done in different sieved martian materials containing the amorphous component, in the hope of identifying its physical state. Investigation of flight data for monotonic variations in coarser grains can also reveal coatings or more generally, zonation, which is potentially linked to alteration processes, and thus can provide information on past surface conditions.

References: [1] Taylor S. R et., (2009) CPS. [2] Achilles C. N. et al., (2017) JGR, 122. [3] Blake D. F. et al., (2013) Science, 341. [4] Leshin L. A. et al., (2013) Science, 341. [5] Maurice S. et al., (2012) SRR, 170,95. [6] Wiens R. C. et al., (2012) SRR, 170, 167. [7] Mckay D. S (1993), LPSC XXIV, 963. [8] Allen C. C. et al., (1998) EOS, 79, 34. [9] Forni O. et al., (2013) Spectrochimica Acta, 86, 61-41. [10] Rapin W. et al., (2017) SAPB, 137, 13-22. [11] Achilles C. N. et al., (2017) JGR, 122.