PROBING CRYS~ALLINE AND AMORPHOUS PHASES AT YELLOWKNIFE BAY, GALE CRATER, MARS: COMPARISON OF CHEMCAM LIBS DATA WITH CHEMIN XRD RESULTS. E. Dehouck1, P.-Y. Meslin1, O. Gasnault1, A. Cousin1, O. Forni1, W. Rapin1, S. Maurice1, R. C. Wiens2, M. Salvatore3, 1Institut de Recherche en Astrophysique et Planétologie (IRAP), Toulouse, France (erwin.dehouck@irap.omp.eu), 2Los Alamos National Laboratory (LANL), Los Alamos, NM, USA. 3University of Michigan-Dearborn, MI, USA.

Introduction: The Mars Science Laboratory (MSL) rover Curiosity embarks a unique suite of scientific instruments capable of characterizing both the chemistry and mineralogy of soils and rocks encountered at Gale crater. This suite includes the ChemCam LIBS (laser-induced breakdown spectroscopy) instrument [1,2], the Alpha-Particle X-ray Spectrometer (APXS) [3] and the CheMin X-ray diffractometer (XRD) [4]. Being able to combine chemical and mineralogical measurements is a powerful capability, in particular when dealing with amorphous phases, which would otherwise be difficult to recognize or characterize by these techniques taken individually.

In addition to allowing quick detection of chemical variations during daily operations of the rover, ChemCam provides a very large dataset (~400,000 spectra as of sol 1500), as well as a very high spatial resolution (at the scale of the laser beam, i.e. ≤500 µm). This study compares chemical trends observed in small-scale LIBS measurements with bulk crystalline and amorphous compositions derived from CheMin and APXS data. Our goal is to take advantage of the high spatial resolution of ChemCam to get insights into some physical properties of soil and rock targets (such as grain size, homogeneity, sorting, and possible occurrence of grain coatings), to identify trace/minor mineral phases undetected by XRD, and to better understand the nature and origin of the ubiquitous amorphous component. We focus here on the data collected at Yellowknife Bay, between sols ~120 and 300.

Data and methods: In a typical ChemCam analysis, a raster of several points is performed on the target, with each point corresponding to 30 laser shots. To remove the contribution from airfall dust deposited on the surface of the target, spectra from the first 5 shots are usually ignored. In this study, we used the remaining 25 spectra separately (“shot-to-shot” data) in order to identify potential signatures of individual grains sampled by only a few laser shots [e.g., 5]. The composition in major oxides was calculated for each spectrum based on a set of known samples [6].

Below we present shot-to-shot compositions from ChemCam analyses of targets belonging to the Sheepbed and Gillespie Lake members of the Yellowknife Bay formation [7]. The mineralogy of the Sheepbed mudstone was determined by CheMin at two drill sites named John Klein and Cumberland [8]. Although there is no CheMin analysis of the Gillespie Lake sandstone, the similarity in bulk chemical composition [7] suggests that its mineralogy may not differ much from the Sheepbed mudstone. We thus included Gillespie Lake in our study in order to investigate the effect of a coarser grain size on the trends observed by ChemCam.

The chemical compositions of the crystalline phases inferred from XRD data are compared with the ChemCam shot-to-shot data on Figure 1. These rocks also contain a significant amorphous component (>20 wt%), the composition of which has been estimated through mass balance calculations using CheMin mineralogy and APXS bulk composition [8-10]. These estimates are presented here for three possible smectite compositions (with half of H2O measured by SAM assigned to them) and with uncertainties propagated using the method described in [10].

Preliminary results: Comparison with CheMin mineralogy. The ChemCam shot-to-shot data show that the crystalline phases identified by CheMin in the Sheepbed mudstone are intimately mixed at the LIBS scale (no pure endmember sampled except Ca-sulfate in veins), which is consistent with the grain size of the rocks (<62.5 µm) being much smaller that the laser beam (~500 µm). However, the point clouds do show some clear trends toward major mineral phases, mainly plagioclase (e.g., high-Al and high-Na points are also high-Si). Less abundant phases such as pyroxenes or olivine do not produce such trends. One exception is sanidine in the K2O vs SiO2 diagram (i.e., high-K points are also high-Si). This is due to the fact that sanidine is the only K-rich phase in the assemblage.

Overall, very few data points display outside of the point cloud, which suggests the lack of coarser grains within the mudstone. However, in the MgO vs SiO2 diagram, a series of data points belonging to the same analysis (target Fury, sol 188) extends outside the point cloud, towards the upper left. These points have high Mg, low Ca and low Si contents, as well as low totals. This suggests that the laser hit a Mg-sulfate, Mg-perchlorate or Mg-carbonate grain (or an aggregate) large enough for the composition to differ significantly from all the other ChemCam analyses of the Sheepbed mudstone. This serendipitous detection suggests that this phase is rare in the Sheepbed mudstone (hence explaining the lack of detection by XRD), although the shape of the point cloud in the MgO vs
SiO$_2$ diagram (numerous low-Si, high-Mg points) may indicate that it is present in more than one target. S-bearing gases were observed during pyrolysis of the Sheepbed samples but their sources are poorly-constrained [11]; if present, a Mg-sulfate or a Mg-perchlorate (through reaction with sulfide) may have contributed to produce these S-bearing gases.

Comparison with estimated amorphous component compositions. Because the amorphous component is probably at least as abundant as plagioclase in the Sheepbed mudstone [8,10], one might expect to also observe trends towards its composition in the ChemCam dataset. However, these trends might not be easily recognizable, because: (1) estimated compositions obtained through mass balance calculations have fairly large uncertainties, especially given the range of possible smectite compositions [10]; (2) the amorphous component is likely Si-poor and volatile-rich, therefore the trends could be masked by those towards Ca-sulfates.

The Na$_2$O vs SiO$_2$ diagram shows a possible trend towards low-Si, high-Na compositions (highlighted by data points in brown on Figure 1) that may correspond to the amorphous component. To verify this hypothesis, the same data points are reported in brown in the other diagrams: they are also consistent with the overall trend observed in the ChemCam dataset, which can not be solely explained by Ca-sulfates or hydrated phyllosilicates.

Comparison between the Sheepbed mudstone and the Gillespie Lake sandstone. As noted previously by [7], the bulk chemical compositions of the Sheepbed and Gillespie Lake members are similar to each other, although the latter has less points with Si contents $\geq$50 wt%. The shot-to-shot data (not shown) reveals a similar dispersion of the points, which suggests that even though Gillespie Lake is coarser-grained (fine to medium sandstone), the difference compared to Sheepbed is not significant at the LIBS scale.

Future work: Our preliminary results suggest that the amorphous component was sampled by ChemCam, which opens the possibility of determining which minor and trace elements are associated with this component. Thanks to the 17 samples acquired so far by Curiosity (15 drills + 2 scoops), we will be able to conduct similar comparisons between ChemCam data and CheMin results for several additional areas of Gale crater.