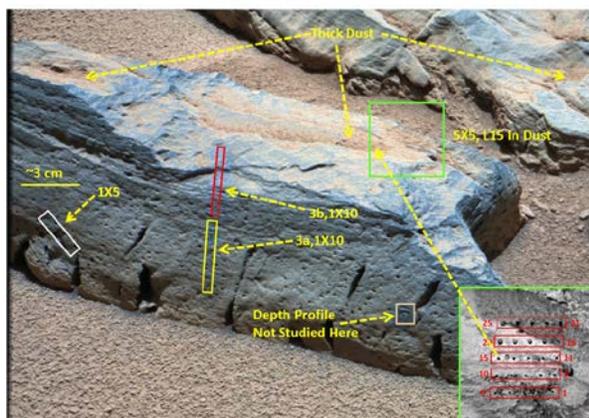


SEARCHING FOR CHEMICAL VARIATION ACROSS THE SURFACE OF “ROCKNEST_3” USING MSL CHEMCAM SPECTRA R.L.Tokar^{1,2}, R.C.Wiens², S.Maurice³, J.Lasue³, J.R.Johnson⁴, R.B.Anderson⁵, A.Cousin^{2,3}, O.Forni³, D.M.Delapp², N.L.Lanza², S.M.Clegg², S.C.Bender^{1,2}, B.L.Barracough^{1,2}, M.D.Dyar⁶, and the MSL Science Team. ¹Planetary Science Institute, Tucson, AZ, USA (rltokar@psi.edu), ²Los Alamos National Laboratory, Los Alamos, NM, USA, ³Institut de Recherche en Astrophysique et Planetologie, Toulouse, France, ⁴Johns Hopkins University, Applied Physics Laboratory, Laurel, MD, USA, ⁵US Geological Survey, Flagstaff, AZ, USA, ⁶Mount Holyoke College, South Hadley, MA, USA.

Introduction. Laser induced breakdown spectroscopy (LIBS) spectra from MSL/ChemCam for the target RockNest_3 (RN3) are studied to investigate the variation in chemical composition across the RN3 surface. Only the dust coating and one laser sample location in heavy dust or sand exhibit a large deviation from the average RN3 composition. However, there are more subtle differences in other LIBS spectra near both rock fracture locations and surface striations that suggest slight felsic or mafic variations and Ca-enrichments likely from Ca-sulfates.

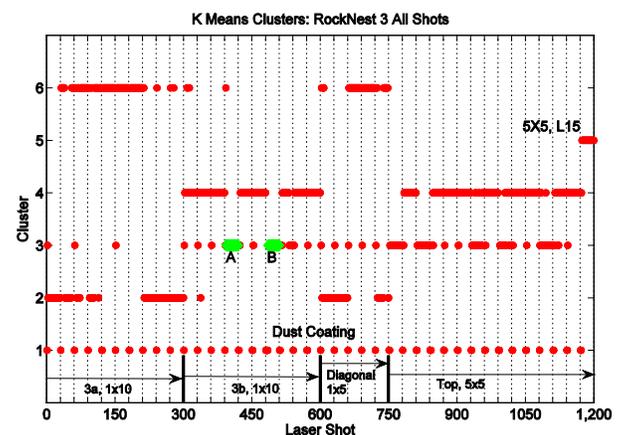
RN3 and ChemCam. A Curiosity MastCam image of RN3 is shown in the following figure, with locations for ChemCam LIBS spectra denoted: two vertical 1x10 rasters (yellow and red), a diagonal 1x5 raster (white) and a square 5x5 raster (green). Each location is hit by 30 ChemCam laser shots (see [1] and [2] for ChemCam instrument details). The top 10 locations for the 5x5 raster (locations 16-25, with 300 shots total, see inset picture) are omitted here as they miss or nearly miss RN3. This leaves 1200 total shots analyzed in this study. Note that location 15 (L15) in the 5x5 appears to be in thick dust or sand (reddish tint); this material is visible on RN3 and neighboring rocks in multiple Curiosity images. The depth profile will be studied elsewhere.



Data Analysis. Two data analysis techniques are combined, k-means clustering and partial least squares (PLS). The ChemCam LIBS spectra contain 6144 wavelengths in the UV (~240 to 340 nm), VIS (~380 to 470 nm) and VNIR (~473 to 900 nm) wave-

length ranges. In k-means clustering the LIBS spectra are randomly assigned to clusters then iteratively moved between clusters until the total sum of distances of the spectra from its cluster center is minimized. The “cluster center” is the average LIBS spectra for the cluster and the distance metric used is the Euclidean distance between spectra with the number of clusters an input parameter. In PLS, predictive models (matrices) are obtained analytically that relate a target’s element or oxide concentration to its LIBS spectra. Here a calibration database of LIBS spectra for known standards is used to calculate the PLS models for each oxide; see [3] and [4] for more details on PLS analysis and ChemCam calibration. Nine oxides are treated: SiO₂, TiO₂, Al₂O₃, Fe₂O₃, MnO, MgO, CaO, Na₂O and K₂O.

The following figure shows, for 6 clusters, the clusters that the 1200 RN3 LIBS spectra populate. For example, cluster 1 contains mainly all 1st shots for each location while cluster 5 contains shots 2-30 for L15 in the top 5x5 raster. The other four clusters contain a mix of spectra from locations across RN3 with average composition differences as indicated by the PLS results in Table 1. The weight percent for the nine oxides are given for the average of all 1200 RN3 LIBS spectra (column 2) and each cluster center (columns 4-9). Note that only the results for clusters 1 (dust coating) and 5 (L15) exhibit large differences from the average and that clusters 2,3,4 and 6 yield similar oxide weight percent concentrations. See [5] for additional detail on the RN3 dust coating.



The following figure illustrates the difference in cluster centers 2 and 4, with labels for the major elements. The results are consistent with the PLS results in Table 1, showing differences in many elements including a reduction in Mg and Ca and enhancements in Si, Al, Na, Li and K. Next detection of enhanced CaO is discussed; see [6] for more detail on ChemCam detection of Ca-sulfates.

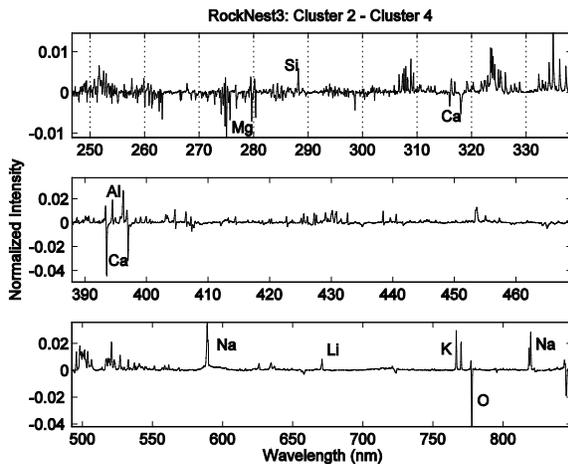
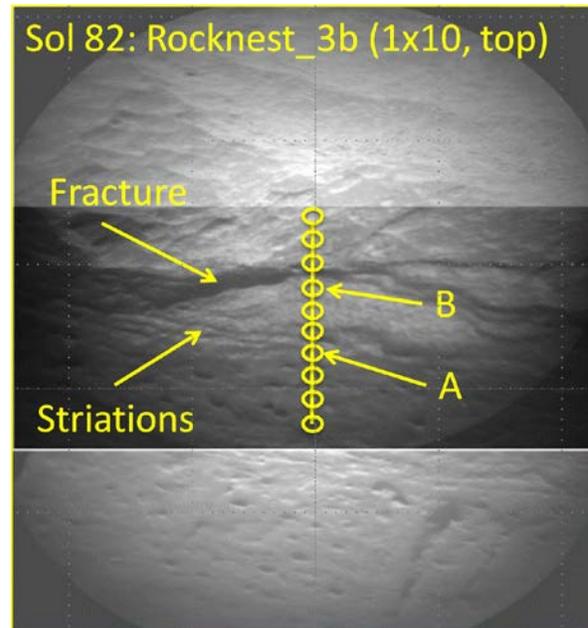


Table 1 indicates that cluster 3 contains spectra with enhanced Ca and Mg, and reduced Si. To search for similar spectra in this cluster, they alone are k-means clustered. Here two groups of spectra that fall into their own cluster are discussed with more details at the meeting. These spectra are labeled A and B in figure 2 above (green points) and are laser shots 394-420 and 486-510. PLS results for these spectra indicate significantly enhanced CaO along with reduced SiO₂ compared to the average RN3 composition. The increase in CaO for groups A and B are ~ +40% and +140% above the mean, with group B having the largest CaO detected over RN3.

These two groups of spectra, labeled A and B, were obtained by ChemCam at locations 4 and 7 in the top vertical 1x10 raster (3b) in Figure 1. This Chem-

Cam raster is overlaid on a ChemCam remote micro imager (RMI) view of RN3 in the following figure. Note that the point A is near the multiple nearly horizontal striations in RN3 while B is near a large rock fracture.



Conclusion. Clustering and partial least square techniques are applied to 1200 ChemCam LIBS spectra for the target RockNest_3. The results are consistent with either a fine-grained sediment or a relatively homogenous tuff deposit, both with Ca-sulfate enrichment in select locations.

References. [1] Wiens et al., Sp. Sci. Rev. 170, 167-227, doi 10.1007/S11214-012-9902-4. [2] Maurice et al., Sp. Sci. Rev. 170, 95-166, doi 10.1007/s11214-012-9912-2. [3] J. Lasue et al. (this meeting). [4] Wiens et al. submitted to Spectrochim. Acta B., 2013. [5] D. Blaney et al. (this meeting). [6] S. Clegg et al. (this meeting).

Table 1: RockNest 3 All Shots

Oxides	PLS AveSpectra (Wt. %)	RMSEP (Wt. %)	Cluster 1 DustCoating Δ (wt. %)	Cluster 2 Δ (wt. %)	Cluster 3 Δ (wt. %)	Cluster 4 Δ (wt. %)	Cluster 5 5X5, L15 Δ (wt. %)	Cluster 6 Δ (wt. %)
SiO ₂	53.1	±6.2	-6.9	+3.2	-3.1	-1.3	-6.2	+4.3
TiO ₂	0.8	±0.6	-0.4	+0.1	-0.2	-0.1	-0.2	+0.1
Al ₂ O ₃	9.7	±2.1	+0.1	+0.3	-0.7	-0.1	-0.3	+0.4
Fe ₂ O ₃ T	27.7	±4.0	-8.4	+0.7	-2.2	+1.3	+9.3	-4.1
MnO	0.2	±0.1	-0.01	+0.02	+0.002	-0.004	-0.03	-0.01
MgO	1.9	±2.2	+3.1	-1.0	+1.6	-0.4	-1.7	+0.5
CaO	3.4	±3.3	-0.5	-0.5	+0.6	-0.4	-2.8	+1.1
Na ₂ O	2.8	±0.6	-1.0	+0.4	-0.4	-0.1	-0.9	+0.4
K ₂ O	0.9	±0.7	-0.5	+0.3	-0.3	-0.1	-1.0	+0.5