

**CHEMCAM SURVEY OF VOLATILE ELEMENTS IN THE MURRAY FORMATION, GALE CRATER, MARS.** N. H. Thomas<sup>1</sup> (nhthomas@caltech.edu), B. L. Ehlmann<sup>1,2</sup>, D. E. Anderson<sup>1</sup>, W. Rapin<sup>3</sup>, S. Schröder<sup>4</sup>, O. Forni<sup>3</sup>, S. M. Clegg<sup>5</sup>, R. C. Wiens<sup>5</sup>, O. Gasnault<sup>3</sup> and S. Maurice<sup>3</sup>, <sup>1</sup>Geologic and Planetary Sciences, California Institute of Technology, Pasadena, CA, <sup>2</sup>Jet Propulsion Laboratory, Pasadena, CA, <sup>3</sup>Institut de Recherche en Astrophysique et Planétologie, Toulouse, France, <sup>4</sup>DLR, Berlin, Germany, <sup>5</sup>Los Alamos National Laboratory, Los Alamos, NM.

**Introduction:** The Mars Science Laboratory (MSL) Curiosity rover is investigating the sedimentary stratigraphy of Mt. Sharp, the mound at the center of Gale crater. Since Sol 753 of the mission, Curiosity has encountered the Murray formation, a fine-grained, thinly laminated mudstone facies which is the lowermost strata of the Mt. Sharp group. As Curiosity traverses the Murray formation, we are using the ChemCam instrument [1, 2] to measure its chemical composition. ChemCam uses Laser-Induced Breakdown Spectroscopy (LIBS) to provide fine-scale (350-550 $\mu$ m diameter) chemical analysis of targets up to 7 m away from the rover and also obtains high-resolution images using the Remote Micro-Imager (RMI). ChemCam is sensitive to the major elements as well as trace and volatile elements, including H, Cl, C, and S.

Hydrogen is an important element in Curiosity's search for evidence of water as it can occur in hydrated or hydroxylated minerals and can be a flag for aqueous alteration or precipitation of water-related minerals. Previously, H has been identified and characterized in a variety of targets using ChemCam [3], and ChemCam analyses of H emission from calcium sulfate veins in the Murray formation indicate a predominance of bassanite [4]. Salts like chlorides, carbonates, and sulphates, found in veins and as cements, are evidence of the aqueous chemistry of past waters and can help us identify depositional units and diagenesis [e.g., 5, 6].

Here we apply the results of recent laboratory LIBS studies characterizing H [7] and Cl, C, and S [8] to ChemCam measurements of the Murray formation to assess the volatile elements present and their variability.

**Methods:** Abundance is proportional to the peak intensities or areas of elemental emission lines in LIBS data. Detection and quantification of H, Cl, C, and S using LIBS are complicated by relatively weak lines, interference with emission lines from other elements, and physical and chemical matrix effects.

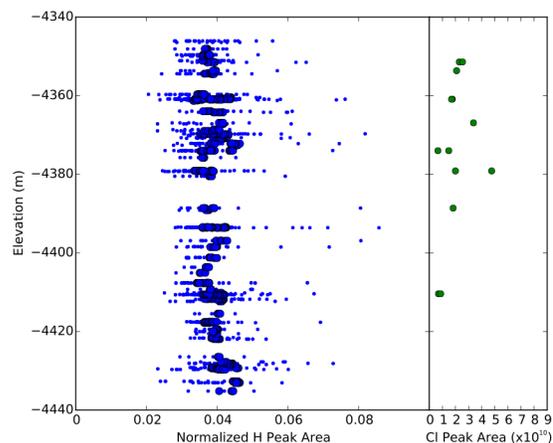
**H Methods.** We used standard ChemCam data pre-processing [9], remove the first five shots (contaminated by dust and subject to surface effects), then fit the local H region (652-662 nm) with two pseudo-Voigt functions (the H-alpha peak at 656.5 nm and the C II peak at 658 nm) and a local linear continuum using a Levenberg-Marquardt least squares minimization algorithm. We estimate error in the fit parameters of peak height and half-width at half maximum (HWHM) using the square root of the diagonal elements of the covariance

matrix. To normalize the H peak, we divide the H peak area by the peak area of O I at 778 nm (fit separately using a pseudo-Voigt). This normalization technique is favored from laboratory studies as it is another neutral atomic emission peak located on the same detector which reduces scatter and produce linear calibrations [7, 10, 11]. In this work, our results are semi-quantitative; we use the normalized H peak area as a proxy for H content. Physical matrix effects (grain size, surface roughness, cohesion, etc.) also influence H emission and are not yet characterized to the extent quantitative calibrations can be extracted for surfaces of highly variable physical properties [3, 7, 10, 11].

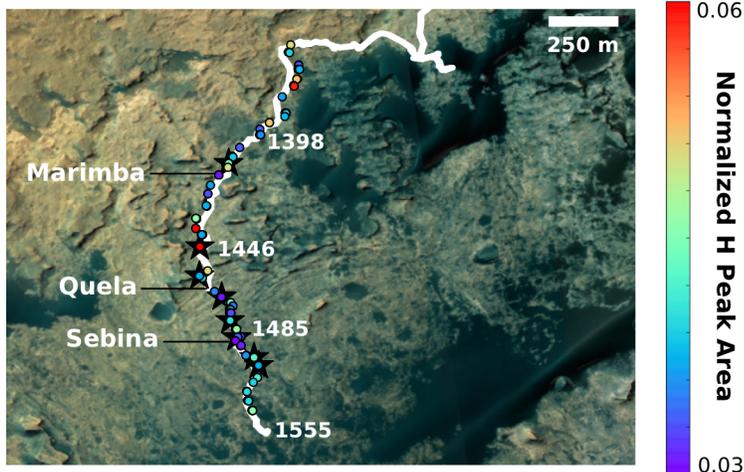
**Cl, C, and S Methods.** Similarly, the first five shots are removed from the CCS pre-processed ChemCam data before peak fitting for Cl. Anderson *et al.* [8] show the Cl emission line at 837.8 nm increases monotonically with Cl content, so we fit this peak using a pseudo-Voigt function and report Cl peak area. We examined all spectra of ChemCam targets measured between Sol 1368-1515 to identify targets containing Cl. To count as a Cl detection, targets must have a clearly visible Cl peak at 837.8 nm and the peak must be higher in intensity than its neighbor at 833.6 nm (a criterion from lab measurements [8]). We are currently working to apply peak fitting methods to C and S emission lines. Anderson *et al.* [8] identified as suitable for semi-quantitative analysis with ChemCam.

**Results:** H emission is detected in all bedrock targets and varies in its normalized peak area (Figure 1). In

**Figure 1:** Normalized H peak area and Cl peak area (where detected) vs. elevation for Murray bedrock targets (Sol 1368-1515). The larger blue points are the 30-point running average.



**Figure 2:** Murray bedrock targets across the recent rover traverse (Sol 1368-1515) overlain on a HiRISE mosaic. The circles are individual ChemCam measurements of normalized H peak area scaled by color from low (purple) to high (red). The black stars are Murray bedrock points where Cl is detected.



general, the normalized H peak area is relatively constant across ChemCam bedrock targets and elevation, but there are outliers with higher H signal throughout the Murray formation. The running average is also plotted in Figure 1 to show more clearly any trends with elevation, or stratigraphic position in the Murray formation. There is no systematic trend with elevation observed for the normalized H peak area, but there are some local decreases and increases. For example, nearby the Quela drill location (~Sol 1446, elevation -4370 m) there is a slight increase in normalized H peak area. This increase can also be seen in Figure 2 as a cluster of red-colored points. Similarly, there are regions of slight decreases normalized H peak area such as nearby the Sebina drill location (~Sol 1485, elevation -4630 m).

We have positively identified Cl in 26 targets measured by ChemCam from Sol 1368-1515. Of these, 12 are Murray bedrock targets while the rest are Cl detections in veins or soils. The fit Cl peak area of the 12 bedrock points are plotted in Figure 1 versus elevation. In the case of Cl, there is a trend with elevation. We have observed Cl more frequently with ChemCam in the recent, higher stratigraphic layers of the Murray formation. An example detection of Cl in a bedrock is shown in Figure 3. In some places, the Murray has nodular texture as seen in Luxilo. Many of the bedrock Cl detections have nodular texture, and there may be an association.

**Discussion:** There are challenges associated with interpreting the normalized H peak area. Changes in measured H could be due to real variation in bedrock wt. % H<sub>2</sub>O or changes in texture because the peak is subject to physical matrix effects. Preliminary work has

found no correlation between normalized H peak area and grain size for Marias Pass targets, but more work needs to be done to understand these effects.

More Cl detections in the higher stratigraphic layers of the Murray likely indicate a higher prevalence of chlorides (high Na is seen in many of these points, so most likely halite) as cementing salts. The chlorides are often seen in nodular textures.

**Future Work:** Currently, we are applying lab-derived methodologies for C and S to ChemCam data from the Murray bedrock. We will evaluate correlations between the volatile elements and the major elements to identify the phases they are in and perform a more detailed study of the morphologies associated with the high H and Cl detections.

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**References:** [1] Wiens, R.C. et al. (2012) *Space Sci. Rev.*, 170, 167-227. [2] Maurice, S. et al. (2012) *Space Sci. Rev.*, 170, 95-166. [3] Schröder, S. et al. (2015) *Icarus*, 249, 43-61. [4] Rapin, W. et al. (2016) *EPSL*, 452, 197-205. [5] Nachon, M. et al. (2014) *J. Geophys. Res. Planets*, 119, 1991-2016. [6] Forni, O. et al. (2015) *Geophys. Res. Lett.*, 42, 1020-1028. [7] Thomas, N. H. et al. (2017) *JGR: Planets*, submitted. [8] Anderson, D. E. et al. (2016) *JGR: Planets*, in revision. [9] Wiens, R.C. et al. (2013) *Spectrochimica Acta Part B*, 82, 1-27. [10] Rapin, W. et al. (2016), submitted. [11] Schröder, S. et al. (2017), in prep.

**Figure 3:** Detection of Cl in ChemCam Luxilo Murray bedrock target. The green circle indicates the LIBS point where Cl is observed. The inset plot shows the observed Cl peak at 837.8nm.

