

CHARACTERIZATION OF HYDROGEN ABUNDANCE IN LIBS DATA. N. H. Thomas¹, B. L. Ehlmann^{1,2}, and D. E. Anderson¹, ¹Geologic and Planetary Sciences, California Institute of Technology, Pasadena, CA (nhthomas@caltech.edu), ²Jet Propulsion Laboratory, Pasadena, CA.

Introduction: Laser Induced Breakdown Spectroscopy (LIBS) provides chemical information from atomic, ionic, and molecular plasma emissions generated by laser vaporization of a sample. The ChemCam instrument on the Curiosity rover uses LIBS to determine geochemical composition. ChemCam fires a pulsed laser beam at a rock or soil target and ablates a 350-550 μm diameter spot [1,2]. The emissions are then observed and recorded by the ChemCam spectrometer over the 240-840 nm wavelength range at high spectral resolution [1,2].

LIBS can detect the presence of light elements including hydrogen. Hydrogen is an important element in Curiosity's search for evidence of water and assessment of habitability. On Mars, water and OH can occur in hydrated or hydroxylated minerals. Recently, analysis of calcium sulfate veins in Yellowknife Bay sedimentary deposits with ChemCam identified a H emission line suggestive of gypsum or bassanite [3]. In addition, H has been found and characterized in dust and soils [4]. Characterizing the degree and style of

aqueous alteration of basaltic materials, including the presence of specific clay minerals, is an important geochemical task for Curiosity and can be aided by analysis of hydrogen with ChemCam data.

While the detection of hydrogen is a straightforward task given one clear emission line at 656.5 nm, quantifying hydrogen content remains a challenge. So far, hydrogen has been detected in most of the targets observed by ChemCam with higher intensities in the soils than the rocks [5]. The abundances of major elements and some trace elements in ChemCam data are being quantified by univariate and multivariate modeling of database reference samples and calibration targets on board the rover, but quantification of H abundance has not been achieved [5]. The goal of this project is to use laboratory samples of mixtures with known, systematic variation in hydrated mineral content and compositionally well-characterized altered volcanics to understand quantitatively how hydrogen emission varies with composition.

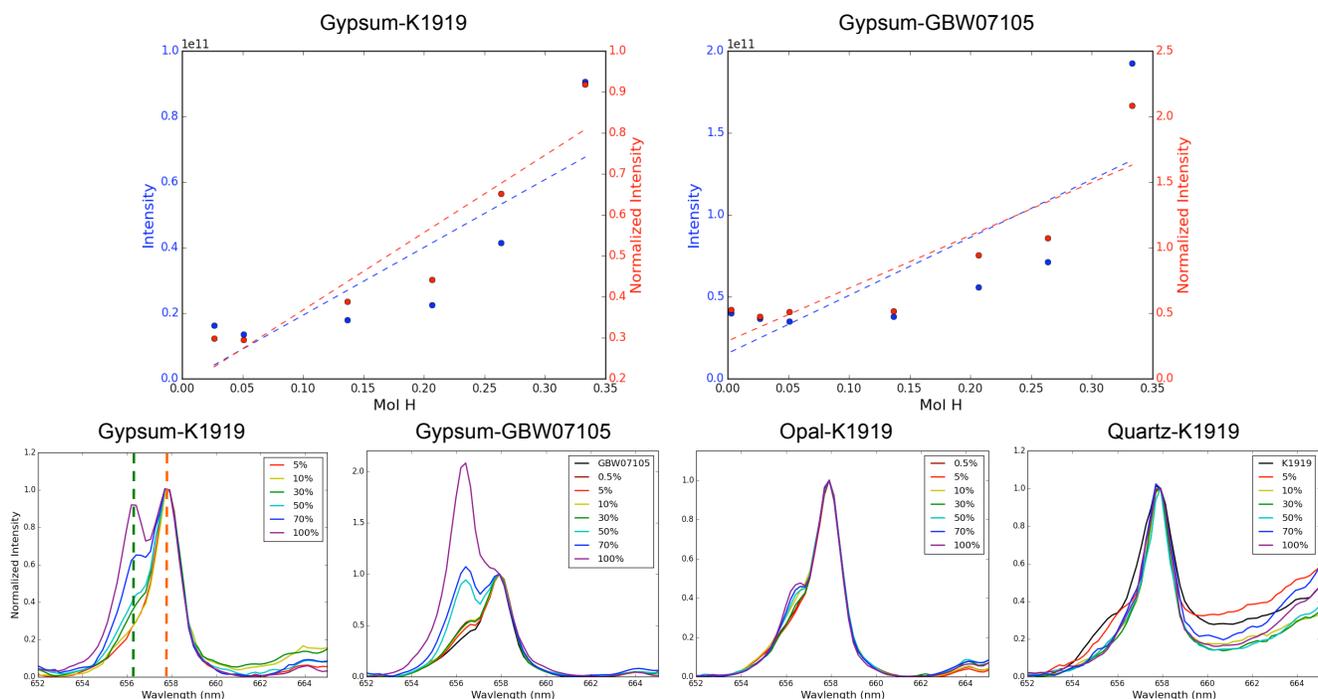


Figure 1: LIBS spectra of the H (656.5 nm, green dashed line) and C (658 nm, orange dashed line) emission peaks for four mixtures. H emission line intensity increases with increasing hydrated phase content (linear fits shown with red and blue dashed lines) when hydrated minerals are present. No systematic trend apparent for the quartz-basalt mixture.

Data and Methods: Oxide- or salt-bearing mixtures with hydrous phases were prepared [6,7]. After powdering ($<<100\ \mu\text{m}$ grain size), mixtures of K1919 basalt and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), quartz (SiO_2), and opal ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$) and a mixture of GBW07105 (higher alkali) basalt and gypsum at 0.5, 5, 10, 30, 50, 70 weight % were pressed into sample pellets for LIBS analysis.

The samples were measured with the LIBS instrument at Los Alamos National Laboratory (LANL), an instrument similar to Curiosity's LIBS instrument. The laser operates at 3 Hz with an energy of 14 mJ/pulse and targets samples at 3 m. The measurements were taken in a Mars-like chamber with 6 mbar of CO_2 . Each sample is targeted at five different points with 50 shots each. Standard ChemCam data processing was applied to the samples: removal of background (measured spectrum with no LIBS), denoising, continuum removal, and wavelength calibration [8].

Preliminary Results: LIBS spectra of laboratory mixtures with hydrated minerals show increasing median peak height with increasing weight percent of the hydrated phase (Figure 1). No systematic trend was observed for the basalt-quartz mixture (Figure 1).

The trend for increase in the median intensity value of the H emission line for all 250 shots across the 5 spots per sample is clearly nonlinear with H mole fraction, estimated based on stoichiometric formula of the hydrated phase (Figure 1). Interestingly, C line intensity also varied, though chamber C line intensity varied, though chamber pCO_2 was constant, so intensities were normalized to the C line at 658 nm for some analyses. The K1919-gypsum mixture shows a systematic increase in C intensity with increasing weight percent, probably indicating a contribution from the H emission.

Investigation of systematic variation in H line intensity over all 250 individual shots (50 per spot) indicates that the median is not capturing the full data variation, however (Figure 2). The first few shots appear to have much higher hydrogen line intensity, though, interestingly, there is also a systematic decrease with shot number at a particular spot, perhaps due to shielding of the plasma by the increasing topography of the LIBS pit. Without normalization to C line intensity, the data for shots 5-50 do not actually show systematic changes in intensity correlated with composition. The shot number and location significantly affect the quantitative relationship between H line intensity and H abundance, so accounting for the processes creating shot-to-shot variation is critical.

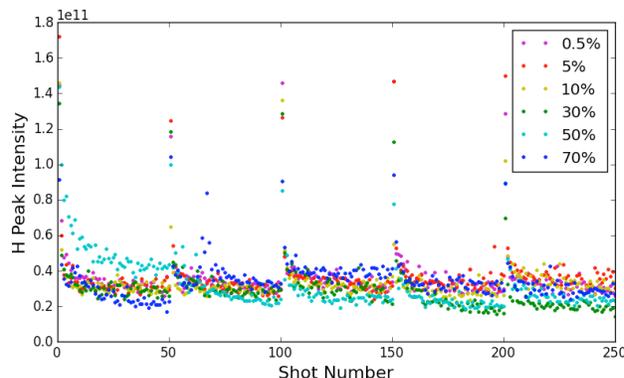


Figure 2: Variation in unnormalized H peak height intensity with shot number for opal-K1919 mixture (colors indicate different weight percent opal). Every 50 shots is a different target location on the sample.

Future Work: Currently, we are using peak height as a measure of the strength of the H and C lines. We plan to fit both the H and C peaks with Lorentzian line shapes to measure the peak area and better account for C and continuum contribution to the H intensity variation. We will apply this method and track both simultaneously to understand the physical processes governing variation in C line intensity and H line emission intensity. In addition, we will apply this method to Mars-analog powders and rocks from altered basalts [9] and basanites [10], representing varying degrees and styles of aqueous alteration that have been well-characterized using independent techniques including XRD, IR spectroscopy, and electron microprobe data [9,10]. Ultimately, our analyses will be extended to martian datasets to provide quantification of H content of martian surface rocks and soils using ChemCam data.

Acknowledgements: Thanks to Rhonda McInroy and the team at LANL for measurement of samples.

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] Nachon, M. et al. (2014) *JGR Planets*, 119. [4] Meslin, P.Y. et al. (2013) *Science*, 341. [5] Schröder, S. et al., submitted *Icarus*. [6] Ehlmann, B.L. et al. (2013) LPSC 44, Abstract #2600. [7] Anderson, D.E. et al. (2015) this conf. [8] Wiens, R.C. et al. (2013) *Spectrochimica Acta Part B*, 82, 1-27. [9] Hadnott, B. et al., in prep. *JGR*. [10] Ehlmann, B.L. et al. (2012) *JGR*, 117.