

CHARACTERIZATION OF HYDROGEN IN BASALTIC MATERIALS WITH LASER-INDUCED BREAKDOWN SPECTROSCOPY (LIBS). N.H. Thomas¹ (nhthomas@caltech.edu), B.L. Ehlmann^{1,2}, S.M. Clegg³, O. Forni⁴, S. Schröder⁵, D.E. Anderson¹, W. Rapin⁴, A. Cousin⁴, P.-Y. Meslin⁴, J. Lasue⁴, D.M. Delapp³, R.E. McInroy³, M.D. Dyar⁵, G.R. Rossman¹, O. Gasnault⁴, R.C. Wiens³ and S. Maurice⁴, ¹Geologic and Planetary Sciences, California Institute of Technology, Pasadena, CA, ²Jet Propulsion Laboratory, Pasadena, CA, ³Los Alamos National Laboratory, Los Alamos, NM, ⁴Institut de Recherche en Astrophysique et Planétologie, Toulouse, France, ⁵DLR, Berlin, Germany, ⁶Mt. Holyoke College, South Hadley, MA.

Introduction: The Mars Science Laboratory (MSL) Curiosity rover is beginning to investigate the sedimentary stratigraphy of Mt. Sharp. Hydrogen (H) is an important element in Curiosity's search for evidence of water and assessment of habitability as it can occur in hydrated or hydroxylated minerals and can be a flag for aqueous alteration. Changes in H abundance along with other chemical indicators show changes in the rock type or environment.

The Curiosity ChemCam instrument [1,2] can identify H quickly and remotely using Laser-Induced Breakdown Spectroscopy (LIBS) and also obtains high-resolution images using the Remote Micro-Imager (RMI). LIBS provides fine-scale (350-550µm diameter) chemical analysis by using a focused laser to ablate target material, generating a plasma which emits light characteristic of composition. While the detection of H is a straightforward task given one emission line detectable by ChemCam at 656.5 nm, quantifying H content remains a challenge. In particular, H is difficult to quantify due in part to an overlapping carbon emission line due to the CO₂-rich martian atmosphere. Previously, H has been identified and characterized in a variety of targets using ChemCam [3]. In addition, ChemCam analysis of H emission from calcium sulfate veins indicates a predominance of bassanite [4].

Goal: The goal of this project is to measure laboratory mixtures with known, systematic variation in hydrated mineral content to understand quantitatively how H emission varies and how factors like chemical matrix effects influence H line reliability, how well the intensity reflects the actual H content. We are also studying compositionally well-characterized altered volcanics with LIBS to relate H to the major and minor elements to assess various degrees and styles of aqueous alteration. This will allow us to measure H in the martian data to characterize the H content and variability and identify aqueous alteration in Gale Crater.

Samples and Methods: Our samples are mixtures of powdered (<100 µm grain size, below LIBS spot size) minerals and Kilauea 1919 (K1919) basalt at 0, 0.5, 5, 10, 30, 50, 70, and 100 weight % mineral. Previously, we characterized the H increase in mixtures of gypsum, opal, and quartz with K1919 and GBW07105 (higher alkali basalt) allowing for matrix comparison [5]. Continuing this work, we selected 6 more minerals containing H: nontronite (standards NAU-1 and NAU-2), brucite, muscovite, serpentine, epidote, and topaz. Nontronite, an Fe-smectite, was chosen as an analog for the orbitally detected Mt. Sharp Fe-phyllsilicate unit. The other minerals were chosen because they have fixed, known H content and passed the following tests: (1) <0.5% mass loss after heating to 200° C (vs. >10% for nontronite), indicating hydroxylated minerals have minimal adsorbed or interstitial H₂O or grungy intermixed hydrated phases, (2) lack of a strong 1.9µm absorption due to H₂O in near-infrared reflectance spectra, and (3) presence of an absorption at 1.4µm due to structural OH.

After being pressed into pellets, LIBS spectra of these mixtures were obtained using the instrument at Los Alamos National Laboratory (LANL) in October 2015 (Figure 1). The laser operates at 3 Hz with an energy of ~14 mJ/pulse and targets samples at 1.5 m. The measurements were taken under Mars-like conditions

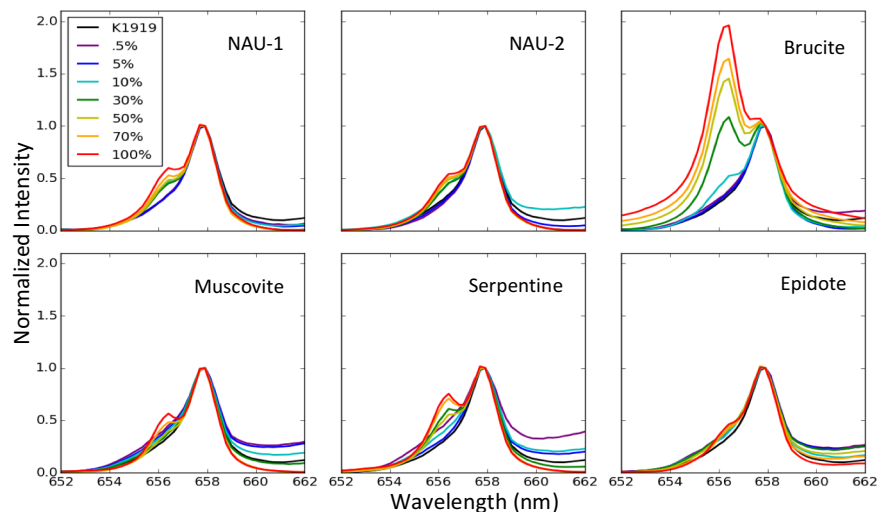


Figure 1: LIBS spectra of the H (656.5 nm) and C (658 nm) emission peaks for mixtures. H emission line intensity increases with increasing mineral content

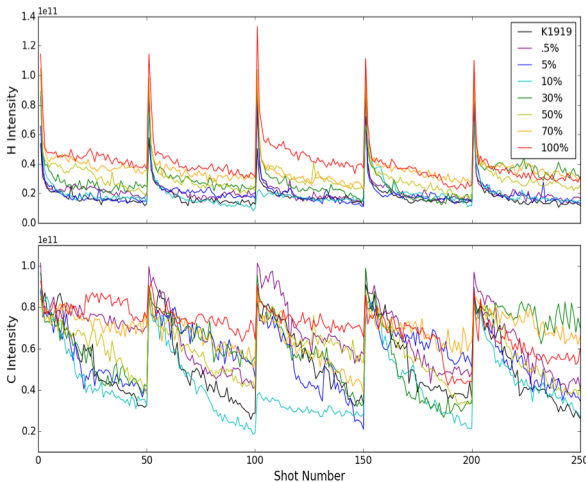


Figure 2: Variation in H peak intensity with shot number for NAU-2-K1919 mixture (colors indicate different weight percent NAU-2). Every 50 shots is a different target location on the sample.

with 6 mbar of CO_2 . Each sample is targeted at five different point locations with 50 shots each. We applied standard ChemCam data pre-processing [6] to our measurements then fit the local H region (652-662 nm) with two pseudo-Voigt functions (the H and C peaks) and a 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.

Results: The peak intensity of both the H peak and adjacent C peak decrease with increasing shot, or laser pulse, number (Figure 2). With the exception of the 50, 70, and 100 wt. % brucite mixtures which show relatively constant, high H intensity across all shot numbers, the first few (~1-3) consecutive shots have much higher H line intensity, and the following systematic,

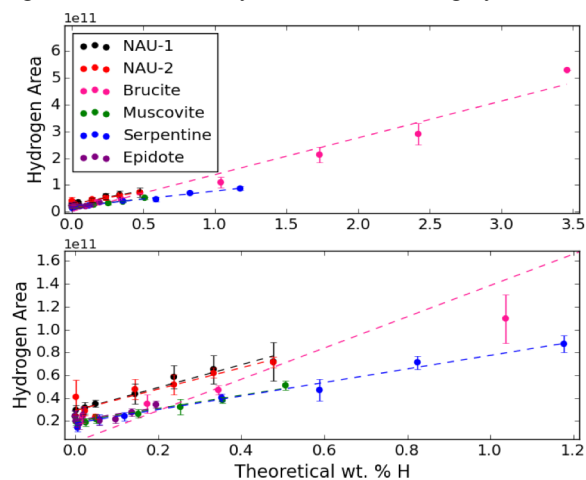


Figure 3: Increase in H peak area with theoretical wt. % H calculated from mineral chemical formula. Dashed lines are best linear fits. Second panel is the first zoomed in to show the lower wt. %s.

slow decrease with shot number is perhaps due to shielding of the plasma by the increasing topography of the laser ablation pit in the sample. Therefore, we used the median of shots 6-50 for peak fitting and analysis. The median better removes random outliers caused by single shot variability than the mean.

We expect the lab chamber to remain at constant pCO_2 , but because laser-target coupling can vary with target texture and composition, C emission might not necessarily remain constant. Empirically, we have found that emission of the C peak at 658nm decreases steadily and can be used for normalization. By dividing by the C area, the H area increases linearly with weight percent H-bearing mineral. We are also testing other methods of normalization including: (1) normalization to total and single detector intensity, (2) normalization to C at 248nm [4], (3) normalization to background continuum [3], and (4) normalization to O at 778nm.

Qualitatively, the H peak height increases with weight percent hydrated mineral in all the laboratory mixtures (Figure 1). When we fit the peaks, there is an increasing trend in H peak area with weight percent (Figure 3). Both the H and C peaks increase with weight percent hydrated mineral, possibly due to differences in laser-target coupling. The brucite ($\text{Mg}(\text{OH})_2$)-K1919 mixture has the most H stoichiometrically, and has a greater rate of H increase with theoretical wt. % than the other mixtures. Epidote has a barely distinguishable H peak area increase (Figure 1) – and it has the least H in its chemical formula.

Future Work: We are also using FTIR and TGA techniques to measure H content of our samples. We will apply our methods to LANL LIBS spectra of powder pellets and rock chips from Mars-analog altered basanites [7] and basalts [8], representing varying degrees and styles of aqueous alteration that have been well-characterized using independent techniques including XRD, IR spectroscopy, and electron microprobe [7,8]. We will compare powder and rock spectra. Our analyses will be extended to ChemCam data to provide quantification of H content of rocks. Measuring H will allow us to test whether the bulk rock is hydrated, and whether it varies in its hydration and thus presumably alteration.

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