LIBS PEAK BROADENING IN SOILS ON MARS.

N. D. Martin[1], H. T. Manelski[2], R. C. Wiens[2], S. Clegg[1], P. B. Hansen[3], S. Schröder[3], and B. Chide[4], [1]LANL, Los Alamos, NM, USA (ndmartin@lanl.gov), [2]Purdue University, West Lafayette, IN, USA, [3]Institut für Optische Sensorsysteme, Deutsches Zentrum für Luft- und Raumfahrt (DLR), Berlin, Germany, [4]IRAP-CNRS, Université Toulouse III, Toulouse, France

Introduction: The chemical analysis technique of Laser-Induced Breakdown Spectroscopy (LIBS) has been successfully used in three separate Mars missions, including NASA's Curiosity rover [1] and Perseverance rover [2, 3], and China's Zhurong rover [4]. LIBS provides elemental compositions of rocks and soils by ablating small bits of a target with a focused laser pulse, then collecting the emitted light from the laser-induced plasma, and organizing it into an emission spectrum through the use of spectrometers. In the case of the Perseverance rover, LIBS is included as a technique of the SuperCam instrument and is used to determine the chemical compositions of rocks and soils in Jezero crater, Mars.

In general, the data of the laser-induced plasma is reliable and interpretable and does not require the time gating typically necessary for use in higher pressure atmospheres such as Earth [5]. A typical measurement consists of 30-50 consecutive laser pulses delivered to the same position before changing to a new raster point. When analyzing soils with LIBS, a small crater is typically formed with which the plasma interacts, potentially influencing the resulting spectra. Here, for the first time, we investigate the progressive broadening of several emission peaks with respect to the number of laser-pulses when targeting soil targets on Mars.

Methods: The LIBS data used in this study includes all geologic targets from Sol 1 to Sol 1000 such that the dataset has a wide variety of chemical compositions and morphologies. The relatively few data points for which the detector was saturated are removed from the dataset. The peaks of interest for this study include Mg at ~280.4 nm, Ca at ~393.5 nm, Na at ~589 and ~590 nm, H-α at ~656.5 nm, K at ~766 and ~770 nm, and O at ~778 nm. The H-α emission peak at ~656.5 nm is included for purposes of calculating electron density, while the other peaks were chosen as they are some of the brightest peaks found in our spectra.

Peak Fitting and FWHM Measurement. To measure shot-to-shot peak broadening, we compare the full width at half maximum (FWHM) of the average spectra of the first five LIBS laser shots on a target to the FWHM of the average of the last five LIBS laser shots on the same target. After the averaged spectra have been calculated, the regions around the peaks of interest are identified. Each peak was fit to a Lorentzian function using the lmfit library available with Python [6]. By utilizing this library, dual peaks seen for Na and K can be fit simultaneously, resulting in a more accurate fit than if the peaks were fit individually. In addition, the lmfit package automatically computes FWHM.

After using this technique, the FWHM values are stored, and the percentage increase in FWHM from the average of the first five shots to the average of the last five shots is calculated. Then, the Lorentzian fits for outliers are plotted and are manually checked for quality of fitting to ensure the data is not skewed by inaccurate calculations.

Results: Figure 1 below shows two examples of the results from the lmfit peak fitting method and FWHM calculation. As seen in Figure 1 (A), peak broadening does not occur at a significant quantity in the rock target. However, in Figure 1 (B), we can see that in the soil target, peak broadening does occur. These behaviors tend to occur in most other targets as well, with little to no broadening occurring in rock targets, and a more significant amount of broadening occurring in soil targets.

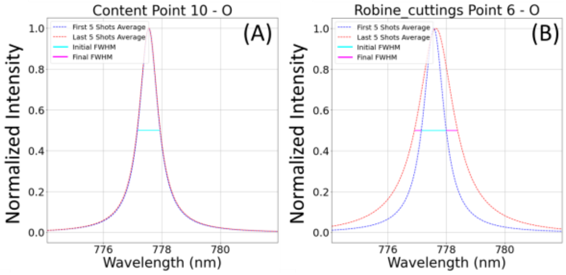

Figure 1 – (A) Normalized peak fits for an O emission peak on a rock target with FWHM values from the averages of the first five shots and the last five represented as lines at 0.5. The peaks and FWHM values are indistinguishable. (B) Same as (A), but for a soil target. Both are normalized to aid in visualization of the shot-to-shot peak broadening. The blue curve represents the fit and the cyan line represents its FWHM for the average of the first five shots. The broader red curve represents the fit and the magenta line represents its FWHM for the average of the last five shots.

Peak Broadening in LIBS: LIBS is a form of atomic emission spectroscopy that uses a laser to produce a plasma consisting of atoms in electronically excited states. These return to a state of lower energy and emit photons that are a characteristic of the elements present.

Doppler Broadening. Due to the thermal motion of the atoms, the light emitted by each particle can be shifted, which can cause emission peaks to broaden in what is known as Doppler broadening, e.g, [7].

However, it has been shown that, in the case of LIBS with the SuperCam instrument, the effect of Doppler broadening is negligible [8].

Stark Broadening. In the thin Mars atmosphere, LIBS plasmas generally exhibit relatively low electron densities and are optically thin. However, there are cases in which the plasma can have a relatively high electron density or can be considered optically thick. High electron density can cause atoms to be perturbed by electric fields due to moving electrons and can result in broadened emission peaks in what is known as Stark broadening [7].

Self-Absorption Induced Broadening. Another phenomenon, self-absorption, occurs in optically thick plasmas in which photons from an emission peak can excite colder material at the edge of the plasma leading to an absorption in the middle of the excitation peak (Fig. 2) [9]. In the case of SuperCam, we do not see this dip in the middle of the peak, but self-absorption could still be occurring to a lesser extent in which the dip is not resolved but instead causing the peak to become flattened, which would contribute to measured peak broadening.

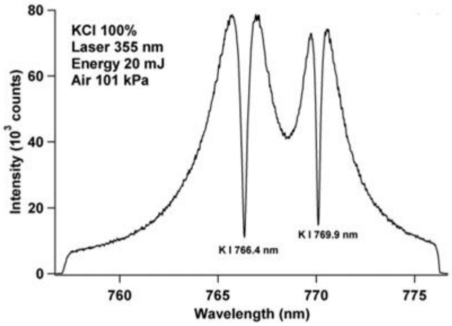

Figure 2 – Example of an extreme self-absorption induced dip in the K doublet with peaks at ~766 nm and ~770 nm, from [9]

Stark broadening can occur in both rock and soil targets, but broadening caused by self-absorption is thought to occur mostly in soils. This is because in soil targets, successive laser pulses can create a small hole that confines the plasma and causes it to appear optically thick (Fig. 3). To test this theory, this study measures the shot-to-shot broadening, then deconvolves the Stark broadening and self-absorption broadening in order to determine which has a larger effect on soils.

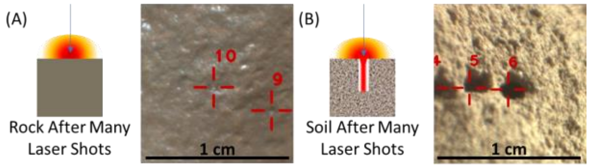

Figure 3 – LIBS plasma characteristics on (A) a hard rock target (Pierrefeu) vs. (B) on a softer soil target (Robine_cuttings). The red color in the diagrams signifies the LIBS induced plasma.

Determining the Cause of Broadening. It has been shown in [10] that the H-α emission peak at ~656.5 nm does not generally exhibit self-absorption. On the other hand, the H-α emission peak is uniquely sensitive to Stark broadening [10]. After measuring the broadening of the H-α emission peak, the electron density of the plasma can be estimated through its relation to Stark broadening, and this electron density can then be used to calculate the estimated Stark broadening in other emission peaks [11]. This value can be subtracted from measured FWHM, and what remains will be due to self-absorption induced broadening even when a central dip is not observed or resolved.

Confirmation with Doublet Line Ratios. In addition to measuring the shot-to-shot progression of the FWHM of multiple emission peaks, we can also confirm the presence of self-absorption in plasma through the use of doublet line ratios. This method involves studying the shot-to-shot ratio of each individual peak within the Ca(II) doublet. If no self-absorption is occurring, the ratio between these peaks will remain roughly constant throughout the shot-to-shot progression. However, if self-absorption is present, this ratio will near the blackbody ratio value of one [12]. This method will be used as a confirmation that self-absorption is occurring in targets, while the FWHM method can be used to quantify the self-absorption that is occurring. Our work on this is in progress.

Perspective of this Work: It is important to study the peak broadening as it may play a role in a variety of LIBS applications. Studying the manifestation of plasma phenomena in LIBS spectra may help improve instrument calibration. So far, there is no evidence of these effects influencing quantification data. However, this work can help ensure robustness to these phenomena in future planetary missions where LIBS may be used.

References: [1] Wiens, R.C. et al. (2012) SSR, [2] Wiens, R.C. et al. (2020) SSR, [3] Maurice S. et al. (2021) SSR, [4] Zhang, Y. et al. (2023) Remote Sens., [5] Wiens, R.C. et al. (2013) SAB, [6] Newville, M. et al. (2023) Zenodo, [7] Bhatt, C. R. et al. (2017) OSTI, [8] Cremers, D. et. al. (2013) Wiley, [9] Karnadi, I. et al. (2020) Sci. Rep., [10] El Sherbini, A.M. et al. (2006) SAB, [11] Manelski, H. et al. (this issue), [12] Hansen, P. B. et al. (2019) EMS