LASER-INDUCED BREAKDOWN SPECTRA OF ROCK POWDERS AT VARIABLE ABLATION AND COLLECTION ANGLES UNDER A MARS-ANALOG ATMOSPHERE. E. A. Breves[1], K. Lepore[1], M. D. Dyar[1], S. C. Bender[2], and R. L. Tokar[2], [1]Mount Holyoke College, Dept. of Astronomy, South Hadley, MA 01075, USA, elly.breves@mtholyoke.edu, [2]Planetary Science Institute, Tucson, AZ 85719, USA.

Introduction: ChemCam on Mars Science Laboratory has analyzed more than 9,000 remote targets with laser-induced breakdown spectroscopy (LIBS) to determine chemical compositions of martian rocks and soils. An advantage of LIBS is that remote ablation, excitation, and collection of atomic emission are possible from different optic-to-target distances and geometries. However, the effects of varying ablation and collection geometry on laser-to-sample coupling efficiency, energy density, reflectance, and alignment of the collection area relative to the spatial distribution of emitting species in the plasma, all of which could affect signal return, are poorly understood. On Mars, ablation and collection angles relative to the rock or soil plane being sampled are highly variable and completely unconstrained. Understanding the effects of sample surface tilt relative to LIBS ablation and collection optics may aid the interpretation of remote data such as those acquired by ChemCam.

Methods: Ten powdered rock standards with compositions ranging from basalt to rhyolite were pressed into 16-mm diameter pellets and placed under a 7-Torr CO_2 atmosphere. LIBS data were acquired in the Mineral Spectroscopy Laboratory at Mount Holyoke College using a 1064-nm Nd:YAG q-switched laser at 10 Hz, 5.6-ns pulse width, and 4 mJ/pulse focused to a 130-µm spot diameter to ablate and excite each sample. A 300-µm, 0.22 NA fiber was positioned one inch above the sample surface to collect plasma emission.

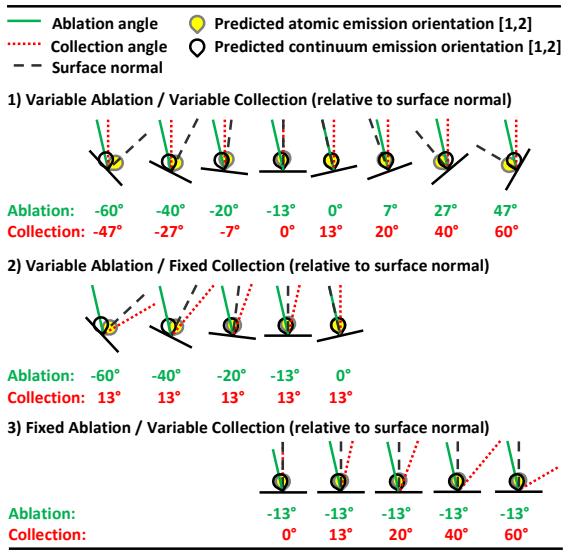

Figure 1. Ablation and collection geometries studied.

Three Ocean Optics HR2000+ spectrometers in UV, VIS, and VIS/near-IR ranges recorded emission in 1-s integrations (10 plasmas per integration) with 5 integrations per location and 6 locations analyzed on each sample. Spectra were acquired 1) while simultaneously varying both ablation and collection angle from -60° to 60°, 2) while varying ablation angle from -60° to 0° keeping collection angle fixed, and 3) while varying collection angle from 0° to 60° keeping ablation angle fixed (**Figure 1**).

Results and Discussion: Total intensity increases non-linearly as ablation/collection angles approach normal to the sample surface for all geometries (**Figures 2** and **3**). This can be explained largely by collection geometry; the atomic and continuum emissions are better aligned under the collection optic at 0° ablation and collection (**Figure 1**). The relative flatness of the variable ablation/fixed collection trend suggests ablation angle has less effect than collection angle for the MHC LIBS, and that the effects of varying ablation angle on beam energy density are minimal for this instrument (**Figure 3**). Signal return for all compositions is most stable between ±20° for all geometries. Higher silica compositions with higher density and refractive index show greater total signal return, though variations in signal return with angle are of similar magnitude for all compositions studied (**Figure 3**).

The ratio of summed emission peak intensity to summed continuum intensity decreases as ablation or collection angle approaches 0° for all geometries (**Fig-**

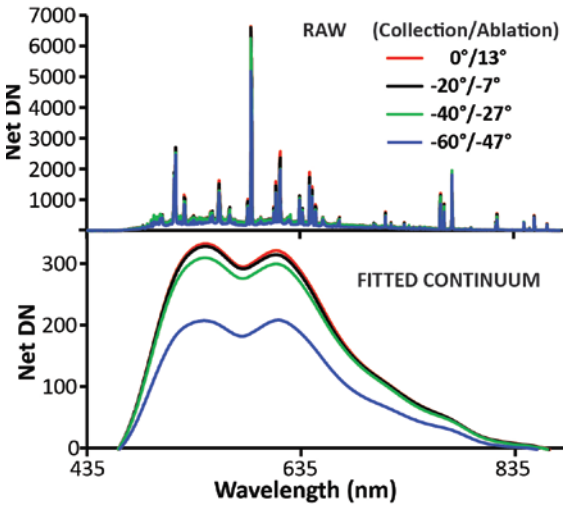

Figure 2. VIS/near-IR spectra of GBW07105 for variable ablation/variable collection geometry showing negative ablation angles only.

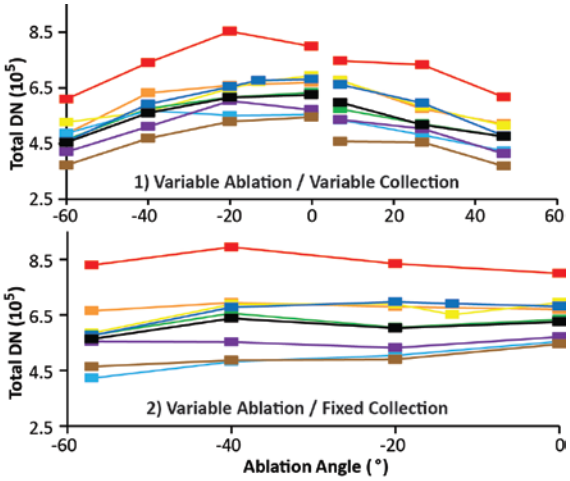

Figure 3. Sum of intensities of all pixels. Warmer colors indicate samples with higher SiO_2 content.

ure 4). Collection alignment alone can explain this trend in geometries 2 and 3; proportionally more continuum emission should be collected as the angle approaches 0° (**Figure 1**). The trend in geometry 1 is opposite that expected from collection alignment. This suggests that continuum intensity increases at a faster rate than atomic emission intensity as ablation angle approaches 0°. Indeed, the sum of pixels of the fitted continuum increases as ablation angle approaches normal for the variable ablation/fixed collection geometry, while sum of pixels of emission peaks is flat or slightly decreases (data not shown).

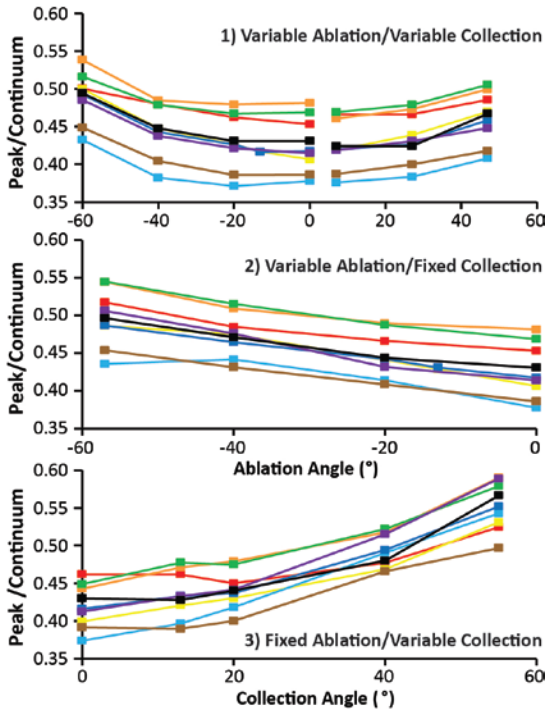

Figure 4. The ratio of summed emission peak intensity (sum of pixel intensities of continuum-subtracted spectrum) to summed continuum intensity.

The ratio of Si(II)/Si(I) (634 nm/288 nm) emission lines can be used as a proxy for variations in spectral shape due to plasma temperature [3] or spatial distribution of species. The flat Si(II)/Si(I) curve for variable ablation/fixed collection suggests incident angle has little effect on species distribution for the MHC LIBS (**Figure 5**). Energy density variation with ablation angle may be minimal due to the small beam diameter (~130 µm). Decreasing Si(II)/Si(I) ratios toward 0° for fixed ablation/variable collection suggest that Si(II) and Si(I) have different spatial distributions within the plasma, and Si(I) is preferentially sampled as collection angle approaches 0°. This is consistent with [2], who found that Al(II) propagates vertically while Al(I) propagates horizontally. If Si behaves similarly, Si(I) could be preferentially sampled as the taller Si(II) plume is excluded from the collection area while rotating the collection fiber about the target.

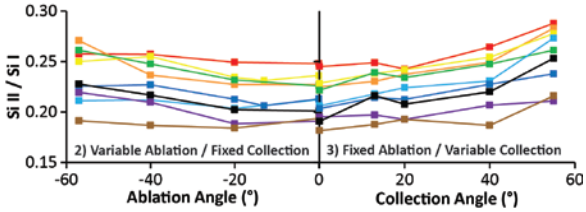

Figure 5. Si(II)/Si(I) (634 nm/288 nm) is used as a proxy for variations in spectral shape due to plasma temperature or spatial distribution of species.

Implications for Remote LIBS: Variation in total signal return, peak-to-continuum ratio, and species distribution with ablation/collection geometry necessitates instrument-specific geometric calibrations to achieve quantitative analyses of compositions from remote LIBS spectra in the lab or on Mars. Signal is most stable within ±20° for the variable ablation/variable collection geometry (most similar to ChemCam geometry), though angles greater than 60° have been employed on Mars. The extent to which uncertainties in elemental compositions predicted by ChemCam arise from these variations is presently unknown. Mars data acquired on the same target at varying ablation/collection angles would begin to assess the magnitude of this effect. A single calibration may be applicable to all compositions encountered, as the basalt to rhyolite compositions studied behave similarly.

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References: [1] Piepmeier E. H. and Malmstadt H. V. (1969) *Anal. Chem., 41,* 700-707. [2] Multari R. A. et al. (1996) *Appl. Spectrosc., 50,* 1483-1499. [3] Tokar R. L. et al. (2015) *LPS LXXVII*, Abstract #1369.