**LASER-INDUCED BREAKDOWN SPECTROSCOPY OF ROCK POWDERS PERFORMED AT VARIABLE ANGLES OF ABLATION AND COLLECTION.** K. H. Lepore[1], E. A. Breves[1], M. D. Dyar[1,2], S. C. Bender[2] and R. L. Tokar[2], [1]Mount Holyoke College, Department of Astronomy, 50 College St., South Hadley, MA 01075, klepore@mtholyoke.edu, [2]Planetary Science Institute, 1700 East Fort Lowell, Suite 106, Tucson, AZ 85719.

**Introduction:** Laser-induced breakdown spectroscopy (LIBS) has become a popular tool in geochemists' toolkits for terrestrial and planetary exploration. However, quantitative analysis of LIBS spectra is plagued by variabilities in collected spectra that cannot be attributed to differences in elemental composition [1,2]. These are likely exacerbated during field work, when the angles of ablation and collection are constantly changing [3]. This study quantifies the uncertainty introduced to element predictions based on LIBS spectra when the actual geometry of field-based measurements is different from laboratory-based conditions. Multiple sampling geometries are used to 1) quantify spectral variability due to changes in LIBS configurations, and 2) isolate the variability in LIBS spectra due to changes in laser ablation angle from those due to changes in the collection angle.

**Experimental setup:** Standards analyzed encompass a diverse collection of rock types, including eight igneous rocks, one forsteritic olivine (DH4911), and one marine sediment (GBW07313) (**Figure 1**).

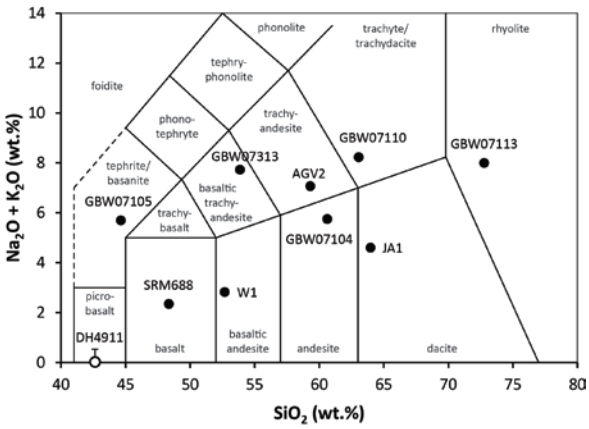


**Figure 1**. Total alkalis vs. $SiO_2$ for standards analyzed.

Standards were shatterboxed, then pressed into uniform pellets for analysis. LIBS data were acquired in the Mineral Spectroscopy Laboratory at Mount Holyoke College (MHC) under Mars atmospheric conditions. A Quantel Ultra100 Nd:YAG q-switched laser operating at 1064 nm was used to ablate and excite each standard. A 400-µm, 0.22 NA fiber optic cable was positioned inside the vacuum chamber 25.4 mm above the standard surface to collect plasma emission. The cable was mounted onto a moving arm that rotates the fiber from 0º to 60º at a fixed distance from the pellet surface. Three Ocean Optics HR2000+ spectrometers recorded plasma emission during 1-s integrations at wavelength ranges of 240-340 nm, 380-470 nm, and 470-880 nm. Four locations were analyzed on each standard with five integrations per location for a total of 200 pulses per standard to mitigate any possible effects of heterogeneity in the pressed powder surface.

Spectra were acquired at a series of discreet angles relative to the target surface normal using three geometric configurations:

1. varying both ablation and collection angle from -60º to 60º, with a fixed 13º angle between ablation and collection (VV),
2. varying ablation angle only from -60º to 0º, keeping collection angle fixed at 13º (VF), and
3. varying collection angle only from 0º to 60º, keeping ablation angle fixed at -13º (FV).

The VV configuration most closely resembles field conditions such as those of the ChemCam LIBS [4] on the *Curiosity* rover. A series of fixed-angle pellet tilt mounts were machined at MHC to position the standard surface normal at several discrete angles ranging

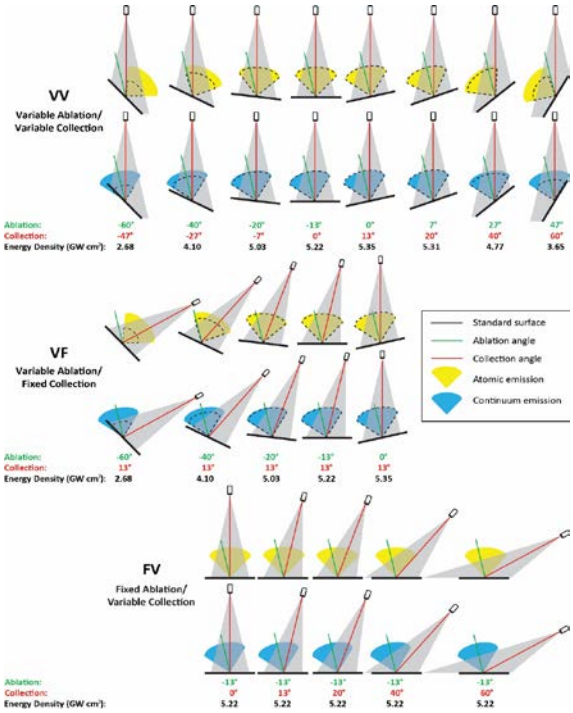


**Figure 2.** Geometries and estimated ablation beam energy densities used for variable angle LIBS measurements. Angles are relative to the standard surface normal. Atomic and continuum emission clouds are illustrated to show the expected orientation of the emission as reported in Multari et al. [3], not the actual size or shape of the plasma. The visible plasma was observed to be perpendicular to the standard surface regardless of ablation angle.

from -60º to 60º relative to the incoming ablation beam (**Figure 2**).

**Results and discussion:** Spectral variations with changing angles are observed using the summed spectral intensity (the sum of all atomic emission lines from 240 nm to 880 nm) and the fitted continua (**Figure 3**). For all spectra, both the continua and summed spectral

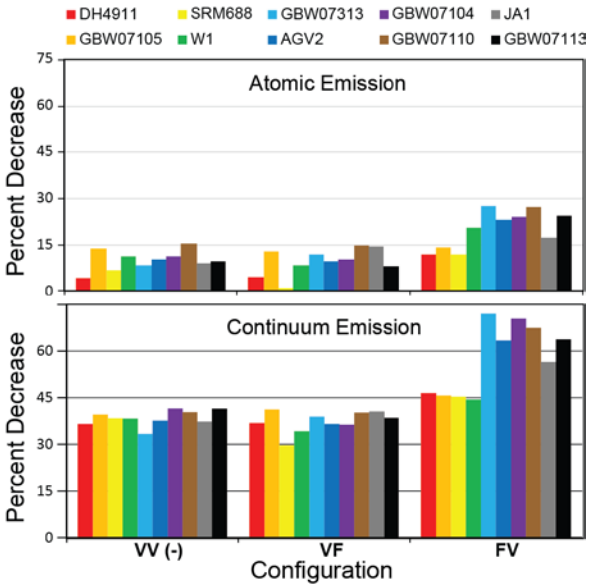


**Figure 3.** Changes in continuum and summed emission intensity from 0º to 60º ablation and collection angles.

intensities increase as ablation and collection angles approach normal to the standard surface. Signal loss in the continuum is 2-4× greater than in emission intensity.

*Relative importance of ablation and collection angles.* In the VV configuration, both ablation and collection angles are changed, but in the VF configuration only ablation angle changes. Therefore, the ratio of VV to VF provides a measure of spectral variability due exclusively to changes in collection angle. Similarly, the ratio of VV to FV illustrates spectral changes due only to changes in ablation angle (**Figure 4**).

VV/VF ratios from 0° to 60° in the VNIR range

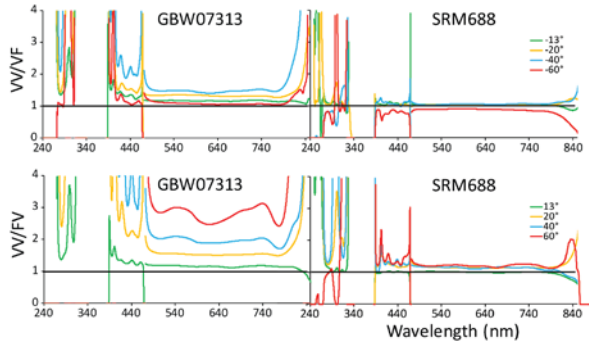


**Figure 4.** Ratios of continua intensities in the VNIR from 0º to 60º.

from approximately 1 to 1.5 for GBW07313, and from 0.85 to 1.1 for SRM688. Small differences in VV/VF ratios among all angles for both basaltic (SRM688) and alkaline (GBW07313) samples imply that changes in the collection angle create minimal changes in the observed spectra. However, VV/FV ratios range from 1.1 to 3.1 for GBW0731 and from 1.0 to 1.2 for SRM688. The relatively large changes in ratio for GBW07313 indicate that 1) changes in the ablation angle are the predominant cause of observed spectral variability, and 2) depending on geochemical composition, some samples are more susceptible to differences in collection geometry than others.

The general trend observed with composition is that Fe/Mg-rich basalts have higher signal return than Si-rich or alkaline rocks. Due to their increased density, basaltic rocks have higher refractive indices that likely improve the laser-to-sample coupling and increase the total ablated material. In addition, spectra collected from basaltic standards change less with changing angles of ablation and collection (Figures 2 and 3) than those of more alkaline rocks.

*Plasma dynamics and changes in collection and ablation angles.* Relative to ablation angle, the effects of variable collection angle are diminished because smaller, less dense plasmas form at large ablation angles and are collected efficiently despite poor collection alignment (**Figure 2**). Smaller plasmas are also more likely to be optically thin, thereby reducing effects of self-absorption [5]. Therefore, the spectra collected in the VV configuration are less variable, especially within ±20º to normal. In contrast, the full effects of varying collection alignment are seen in the FV configuration, in which ablation angle is fixed and the plasma remains stable (**Figure 3**).

**Implications:** Elemental compositions of our data predicted using a larger but conventionally-collected calibration suite show that accuracy generally suffers when the ablation and collection angles are high, even when spectra are normalized to total counts for each detector. The magnitude of this effect observed in our limited experiment is 11-19% for $Fe_2O_3$, Ca, and $Al_2O_3$, 2-3% for $K_2O$, $SiO_2$, and $TiO_2$, and negligible for MgO. Optimal quantitative analysis of LIBS spectra must include some knowledge of the angle of ablation and collection so the approximate increase in uncertainty introduced by a departure from normal angles can be accurately reported.

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**References:** [1] Clegg S. M. et al. (2009). *Spectrochim. Acta, Part B, 64*, 79-88. [2] Anzano J. M.et al. (2006). *Analytica Chimica Acta, 575*, 230-235. [3] Multari R. A. et al. (1996) *Appl. Spectrosc., 50*, 1483-1499. [4] Wiens R. C. et al. (2013) *Space Sci. Revs., 170*, 167-227. [5] Diaz Place D. M. (2013). *J. Quant. Spectrosc. Rad. Trans., 129*, 254-262.