TEMPORAL CHANGES IN LIBS SPECTRA OBSERVED USING TIME-SERIES COLLECTION PROTOCOLS. K. Lepore[1] and M. D. Dyar[1], [1]Mount Holyoke College, Department of Astronomy, 50 College St. South Hadley, MA 01075, klepore@mtholyoke.edu.

Introduction: Laser-induced breakdown spectroscopy (LIBS) is an established technique used to measure the chemical composition of geological materials. However, quantitative use of LIBS is hampered by spectral changes that cannot be attributed to differences in sample composition. Sources of variability observed in LIBS spectra include differences in the sample matrix and collection protocols that determine the observed plasma characteristics. Here we address two critical questions regarding protocols for light collection times and gating. First, how are temporal changes in LIBS plasmas manifested in the observed spectra? Second, does the temporal evolution of a LIBS plasma depend on atmospheric conditions?

Instrumentation and methods: LIBS spectra were collected on a set of ten standards at increasingly longer gate delay times to observe temporal changes in plasma characteristics. Standards represent a diverse collection of rock types, including eight igneous rocks, one forsteritic olivine (DH4911), and one marine sediment (GBW07313). Standards were shatterboxed to ensure uniformity, then pressed into pellets for LIBS analysis.

Spectra were collected using the new SuperLIBS instrument at Mount Holyoke College [1], with single-shot capabilities in the UV (240-340 nm), VIS (382-470 nm), and VNIR (600-780 nm) wavelength ranges. In the VNIR range, SuperLIBS is equipped with a PI-MAX4 camera (Princeton Instruments) with intensifier, allowing a time-series of single-shot spectra to be collected at 200 ns intervals throughout the plasma lifetime.

LIBS spectra were collected at ten different gate delay times ranging from 26 to 1826 ns. In the UV and VIS regions, single-shot spectra were collected during 10 ms integration times. In the VNIR, only a snapshot of the plasma was collected during a gate width of 200 ns. A trigger pulse sent by the laser to the VNIR, VIS, and UV cameras ensured that light collection began after plasma formation. Spectra were collected under Mars (7 Torr CO_2), vacuum (100-400 mTorr), and Earth atmospheres at 2.5 mJ laser energy. After acquisition, raw spectra were processed by dark subtraction, wavelength calibration using a Ti standard, and multiplication by an instrument response function. When spectra are normalized, individual intensities are divided by the sum of intensity in each spectral region (UV, VIS, or VNIR).

Results: Spectral changes throughout the plasma lifetime are observed using time-resolved LIBS (Figures 1 and 2). Ionized species of major elements are much more abundant at shorter gate delays, while neutral species become prominent at longer gate delays (Figure 1). For example, Si(II) and Mg(II) peaks are predominant early in the plasma and are reduced at longer gate delays, when Mg(I) intensity increases.

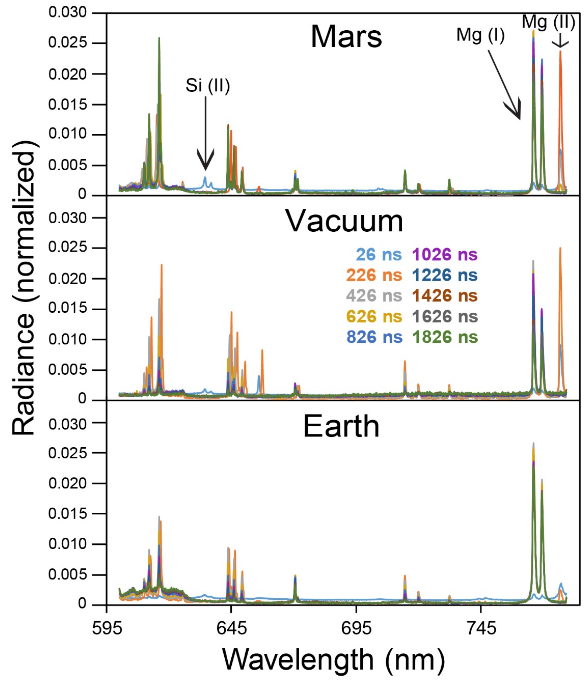

Figure 1. VIS-NIR spectra collected at 200 ns intervals between 26 and 2026 ns.

The relative abundances of more highly ionized species such as Mg(II) and Si(II) are often used as a proxy for plasma temperature [2]. In these time-gated spectra, Si(II) and Mg(II) peaks exist at longer gate delay times in collections in a Mars-like atmosphere than in vacuum or Earth conditions (Figure 1). In contrast, neutral Mg(I) peaks reach maximum intensity earliest under Earth atmosphere (426 ns), indicating the predominance of neutral species under a higher-pressure environment.

Time-delay trends of plasma characteristics. Trends in summed radiance for the VNIR spectral region fall into three "series" under Mars atmosphere, and two "series" under vacuum and Earth atmospheres (Figure 2). In all atmospheric conditions, Series 1 is characterized by high VNIR radiance and high II/I ratios of Si and Mg. Under vacuum and earth atmospheric conditions, radiance decreases by 200 ns and remains low throughout the rest of the plasma lifetime. However, VNIR radiance increases between 600 and 1600 ns under Mars atmospheric conditions. This is likely an optimal time for

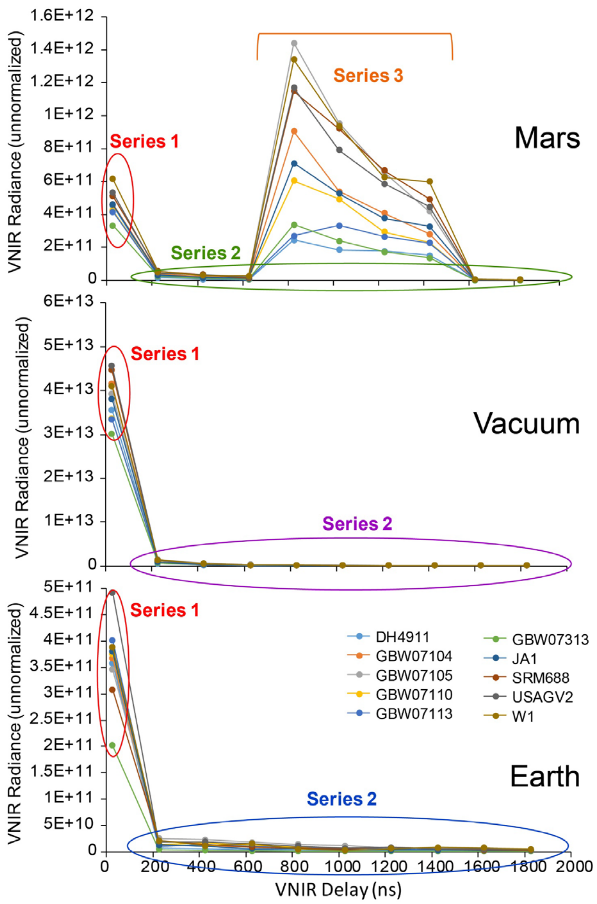

Figure 2. Time series of summed spectral radiance in the VNIR wavelength region under Mars, vacuum, and Earth atmospheric conditions.

spectra collection due to high peak radiance and little interference from Bremsstrahlung radiation.

Implications for LIBS spectra collection: The "series" observed throughout the plasma lifetime under all three atmospheric conditions are distinguished by the slope of the linear relationship between VNIR intensity and Si(II)/Si(I) ratios (plasma temperature) (**Figure 3**). High-intensity spectra under Mars atmosphere and vacuum exhibit similar linear relationships with plasma temperature (pink and orange). A similar correlation exists between low-intensity spectra and plasma temperature under Mars and Earth atmospheres (blue and green), but slopes of these linear relationships are 2-3 orders of magnitude greater.

Relatively high-intensity spectra collected in Mars atmosphere or vacuum conditions demonstrate greater spectral variability with changes in plasma temperature (Figure 3). In contrast, low-intensity spectra collected under Earth atmospheric conditions are less sensitive to changes in plasma temperature. One explanation is that observed radiance is reduced at high temperatures due to self-absorption in the plasma. This is especially likely under Earth conditions, where electron density is higher due to ambient gas concentrations [3,4]. The reduction in peak radiance observed in early (226-626 ns) measurements under Mars conditions may also be attributed to enhanced self-absorption in the early plasma.

Substantial changes in spectral intensity and plasma temperature (indicated by Si(II)/(I)) demonstrate that choice of gate delay time in collection protocols has a profound impact on peak intensity and distribution of collected spectra (Figures 1 and 2). Under Mars atmospheric conditions, data collected between 600 and 1600 ns are optimal for LIBS analysis due to enhanced signal

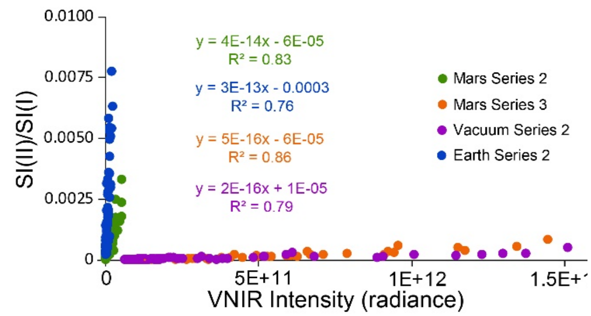

Figure 3. Si(II)/(I) ratios plotted against the summed spectral intensity in the VNIR wavelength range.

to noise ratios, relatively high peak intensities, and diminished Bremsstrahlung continuum emission [3,5].

Even when Si(II)/Si(I) ratios are matched between two sets of LIBS spectra, if these are collected at different times in the plasma lifetime, the relationship between plasma temperature and spectral intensity may not be equivalent (Figure 3). In this case, other criteria, such as peak broadening due to electron density, should be considered to ensure that plasma conditions are similar enough to allow a comparison between spectra.

In conclusion, gate delay times must be taken into account in order to acquire similar peak distributions across different LIBS instruments. This is especially critical under Mars atmospheric conditions, where three unique "series" exist during a single plasma lifetime (Figure 2). Collection protocols used for calibration suites should be matched to those used for unknown samples to improve spectral similarity and the accuracy of element predictions.

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References: [1] Lepore K. et al. (2018) *LPS XLIX*, Abstract #1179. [2] Tokar R. et al. (2015) *LPS XLVI*, Abstract #1369. [3] Cremers D. A. and Radziemski L. J. (2006) *Basics of the LIBS Plasma*, John Wiley and Sons, Ltd., England. [4] Glumac N. and Elliott G. *Opt. Lasers Eng.*, *45*, 27-35. [5] Anabitarte F. et al. (2012) *ISRN Spectroscopy*, *2012*, Article ID 285240.