A PRELIMINARY EXAMINATION OF METEORITES WITH LASER-INDUCED BREAKDOWN SPECTROSCOPY (LIBS)

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Introduction: Laser-induced breakdown spectroscopy (LIBS) is an emission spectroscopy technique used to determine the elemental composition of a target material. This technique uses a pulsed laser to create a plasma on the surface of the target, which in turn emits light of wavelengths characteristic of the constituent species [1]. The first LIBS instrument for extraterrestrial applications has been selected as part of the ChemCam instrument package onboard the 2011 Mars Science Laboratory (MSL) rover Curiosity. Because the LIBS technique is particularly well suited to low pressure and vacuum environments [2], LIBS has also been proposed for future missions to the Moon and asteroids [2, 3].

In this preliminary study, a suite of meteorite samples are examined with LIBS under low pressure with low laser power in order to better understand how these materials might appear to a LIBS instrument on the surface of an asteroid. Of particular interest is distinguishing between meteorite types. Although only one asteroid, Itokawa, has been directly sampled (e.g. [4]), meteorites represent asteroidal materials from many asteroids covering a wide range of compositions. Previous workers have examined a number of individual meteorites with LIBS in a variety of environments (e.g. [5-7]); most samples in this study are measured for the first time with the LIBS technique.

Sample suite: Eleven meteorites were examined in this study as examples of potential compositions for asteroidal bodies (Table 1); a range of material types were selected and all are well characterized in the literature. In addition to the meteorite samples, a standard of Fe metal was also measured for comparison to samples containing significant quantities of Fe-metal.

Table 1. Meteorite samples used in this study

Name	*Type*
Olivenza	LL
Oliver	L
Bruderheim	L6
Leoville	CV3
Abbott	H6
Happy Canyon	EL 6/7
Palo Blanco	Eucrite
Bondoc	Mesosiderite
Admire	Pallasite
Canyon Diablo	1AB
Canyon Diablo graphite nodule	1AB
Zagami	Shergottite

Methods: *LIBS.* A Spectra Physics Indi Nd:YAG laser operating at 1064 nm, a repetition rate of 10 Hz, and an energy of 15 mJ/pulse was used to probe the samples as described in [8]. The laser beam was focused onto the sample surface, which was positioned at a standoff distance of 4 m. Samples were analyzed under 7 Torr CO_2 to simulate collection of data in a low-atmospheric pressure environment. Some of the plasma emission was collected with a telescope and then directed through a demultiplexer connected to three Ocean Optics HR2000 spectrometers, each covering a different spectral region ranging from ~230-800 nm (UV, VIS, and VNIR). The integration time was set to 1 s such that the emission from 10 spectra were recorded in in spectrum, and five spectra were averaged for each LIBS spectrum such that each recorded spectrum is the combination of 50 laser shots. Three locations on individual samples were sampled, and three 50-shot spectra were collected in each sampling location; all shots collected for a single sample were then normalized to the total emission intensity and then averaged to obtain a bulk composition for each individual sample so that each sample spectrum is composed of between 250-450 laser shots.

PCA. Principal component analysis (PCA) was used to analyze and classify the LIBS data [8, 9]. PCA helps to reduce the number of significant dimensions within a data set and is a measure of spectral variability; rocks with similar compositions will plot together in PCA space. The PCA model was built using the commercial software Unscrambler.

Results: The PCA model suggests that differences in Fe, Ti, Na, and Ca content account for the majority of variation between the selected meteorite samples (Fig. 1). Samples with the most Fe plot near one another, with the presence of Fe metal having a strong effect on where samples plot within PCA space. However, additional elements such as Mg and Al also control the placement of individual samples within the model to a lesser extent. The pallasite Admire plots well within the Fe-rich region despite having a large silicate component; this is likely due to the strong coupling of the Fe-Ni matrix with the laser. The spectrum for Canyon Diablo, an iron meteorite, and the Fe metal standard were extremely similar as expected, plotting almost on top of one another in this PCA model. In addition to Fe, Canyon Diablo also contains Ni, which has several overlapping spectral lines with

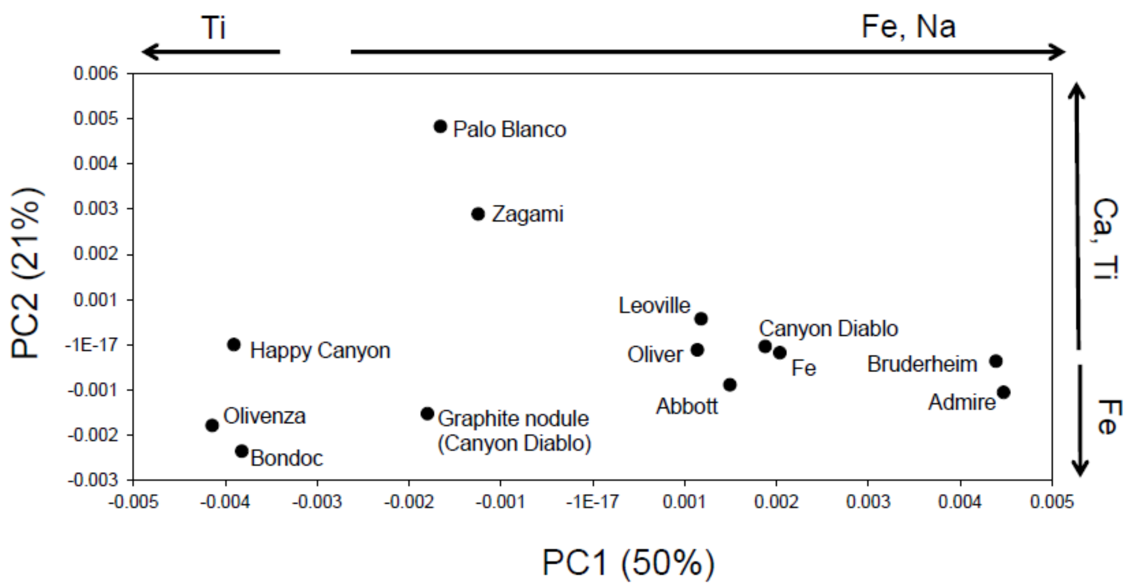

Fig. 1. Principal component analysis (PCA) scores plot. PC1 and PC2 represent 50% and 21% of the total spectral variation, respectively. PC1 is most strongly influenced by Fe and Na (+) and Ti (-), while PC2 is most strongly influenced by Ca and Ti (+) and Fe (-). Although meteorites such as Olivenza and Bondoc are not particularly Ti-rich, they contain Ti peaks that set them apart from the Fe-rich meteorite group along the PC1 axis.

Fe. The strongest emissions for Ni are generally found ~340-350 nm (e.g. [1]), a spectral region in which the current laboratory setup does not have coverage. In order to better differentiate between Fe and Ni in this sample, the spectrum of Fe was subtracted from that of Canyon Diablo. Several emission lines that correspond to Ni appear in Canyon Diablo and are absent in the Fe standard (Fig.2).

These data represent a first attempt to measure, discriminate between, and interpret meteorite samples with LIBS in a low-pressure environment. Future work will repeat these measurements under vacuum and with higher resolution spectrometers, and will employ additional statistical analysis techniques such as partial least-squares regression (PLS) to quantify meteorite compositions.

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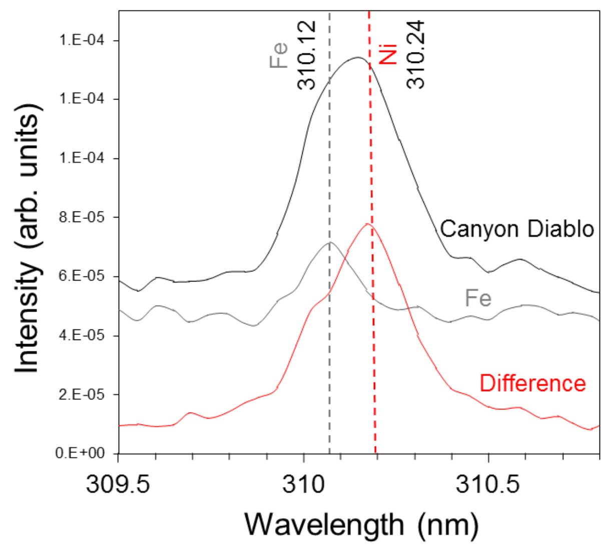

Fig. 2. LIBS spectra of the Canyon Diablo meteorite (top, black), an Fe-metal standard (middle, grey), and subtraction of Fe from Canyon Diablo (red, bottom). Both Fe and Ni have peaks ~310 nm; in the Canyon Diablo spectrum this appears as a peak with a shoulder on the left and as a single Fe peak in the Fe spectrum. When the Fe spectrum is subtracted from the Canyon Diablo spectrum, the location of the nearby Ni peak is revealed at 310.24 nm. Note that wavelengths listed are for vacuum.