INTRODUCTION: Recently, LIBS (Laser-Induced Breakdown Spectroscopy) has been proposed as a new method for elemental analysis in space exploration with Mars specifically targeted. There are many reasons for this including rapid analysis (<2 min.), in-situ and stand-off analysis (<20 meters) capability, and the ability to readily combine LIBS with other spectroscopic methods (Raman, fluorescence) to provide data complementary to LIBS. In comparison with past and current elemental analysis methods used on planetary surfaces, these capabilities of LIBS should greatly increase the scientific return from future missions. We are characterizing the LIBS method for space exploration applications with emphasis on analysis at reduced pressures (~7 Torr CO₂ for Mars) and near vacuum (50 mTorr for asteroids and the Moon; at pressures below about 50 mTorr no significant changes in the plasma are observed).

This characterization is important because the excitation properties of the LIBS plasma are strongly dependent on pressure of the surrounding atmosphere [1,2]. Topics addressed include: (1) calibration curves and detection limits for major and minor elements of interest to geochemistry at the two lower pressures as well as atmospheric pressure (for comparison), (2) using short (<22 cm for in-situ) and medium length (4 m for stand-off) light paths for analysis, and (3) characterization of the LIBS plasma at different pressures.

LIBS Overview: LIBS uses a pulsed laser beam to remotely analyze sample areas up to ~1 mm dia. at distances up to 20 m from the instrument by observing the characteristic spectral lines in the induced laser plasma. The spectral information is useful to identify elements (for rock type identification) and for quantitative analysis. Each laser pulse yields a complete spectrum. A number of spectra are typically averaged together for greater accuracy and precision and to average out composition inhomogeneities.

LIBS can be used to monitor all elements with detection limits in the range of 1-500 ppm typical for many elements. Elements commonly observed in terrestrial soils include H, Be, Li, C, O, Na, Mg, Al, Si, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Sr, and Ba. Other elements such as B, N, S, Ag, As, Sn, Rb, Cs, Ce, Pb, and U have also been seen in certain soils, and still other elements can be observed if they exist at sufficiently high concentrations.

The fact that LIBS can analyze samples remotely increases the number of measurements that can be carried out per unit time, as contact or in-situ techniques can require hours to position the rover adjacent to the sample. As a result, the number of individual LIBS measurements that can be carried out on distinct samples is much greater than the number provided by past (XRF) currently deployed methods (APXS). Stand-off analysis is an advantage that LIBS shares with other remote techniques such as visible, IR, or thermal spectroscopy. LIBS, however, provides high quality elemental composition information that surpasses, in many ways, and complements in other ways, these techniques.

Spark at Different Pressures: As shown in Fig. 1, the appearance of the plasma is significantly different at atmospheric pressure than at 50 mTorr. The difference in appearance is due to the effect of air pressure on the spark; ambient pressure around the spark confines the most luminous portion near the target surface, causing it to occupy a small volume (typically 0.01-0.02 cm³) at atmospheric pressure. The lack of pressure at 50 mTorr allows the spark to disperse and lengthen, as shown at the left, reducing the overall intensity, and reducing in size the most strongly emitting (bright white) area. These differences have implications for the method of light collection (e.g. bare fiber vs. imaging on fiber end) to be employed at difference pressures.

**Figure 1.** (left) LIBS plasma at low (50 mTorr) and (right) high (585 Torr, Los Alamos atm. pressure) pressures formed on an Al plate.

Pressure Dependence of Emissions: The data in Fig. 2 show the dependence of element emissions (peak intensities) on pressure for soil samples maintained in an atmosphere of CO₂. The plasma light was collected by a fiber optic positioned about 22 cm from the sample. These data were normalized for each element at 90 Torr. As the pressure decreased, the emission intensities either remained
constant or decreased slowly (except for Al, and a neutral Ca line) for pressures down to about 5 Torr. The observed increase in intensities for the Al and the Ca(I) lines is an artifact due to self-absorption. Below 5 Torr all element emissions decreased significantly as the pressure was reduced to the minimum pressure examined here (50 mTorr). The loss of signal at pressures below 5 Torr has implications for the use of LIBS on airless bodies and indicates that long stand-off distances (up to 20 m), such as those possible on Mars, may not be possible or that more efficient light collection and recording methods will be required. For comparison, as noted previously, as the pressure is increased above 90 Torr, emission intensities decrease as atm. pressure is attained [3].

**Calibration Data:** The Ba calibration curves in Fig. 3, obtained at three different pressures, were prepared using a series of certified samples containing a suite of elements. Similar curves were prepared for other elements including Mn, Sr, Li, and Cr. Data were collected at 4 meters. Each data point is the average of light from 100 plasmas. At high concentrations, the Ba curves show a relative loss in intensity due to self-absorption of the strong 455.4 nm Ba line. A linear calibration curve can be obtained at higher concentrations through the use of a weaker Ba emission line. Comparison of the curves shows a systematic decrease in the slope of the curve (the analytical sensitivity) with decreased pressure. This was observed for other elements, indicating the need for enhanced instrument capabilities at lower pressures.

**Ablation Rates:** Repetitive sparking at the same point on a sample is useful to remove weathered layers and to bore into the sample to access the bulk composition. Figure 4 shows the number of laser pulses required to completely ablate through basalt and limestone slabs (2 mm thick) and for comparison, an aluminum plate 1.56 mm thick. Each measurement at a certain pressure was carried out a different spot on the sample. This accounts for the variation in the basalt data at the lower pressures. The basalt was visually different at different locations, suggesting variations in composition that may affect the hardness and ablation properties of the target at that position. To the eye, the limestone appeared more homogeneous, and more monotonic data was obtained with this sample. Here, the pulse energy was 60 mJ and laser repetition rate was 10 Hz.