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Title:

Libs-Based Detection Of Geological Samples At Low Pressures (<0.001 TORR) For Moon And Asteroid Exploration

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LIBS-BASED DETECTION OF GEOLOGICAL SAMPLES AT LOW PRESSURES (<0.0001 TORR) FOR MOON AND ASTEROID EXPLORATION. R.D. Harris[1], D.A. Cremers[2], C. Khoo[3], and K. Benelli[3]; [1]Los Alamos National Laboratory, Group EES-2, Los Alamos, NM 87545, [2]SDN Research, 1111 Piedra Rondo, Santa Fe, NM 87501 (Davidsantafe@aol.com), [3]Los Alamos National Laboratory, Group C-ADI, Los Alamos, NM 87545.

Introduction: LIBS is under development for future use on surface probes to Mars [1-3]. Under simulated Mars atmospheric composition and pressure (7 torr, predominately CO_2), LIBS has been shown useful for qualitative and quantitative analysis of geological samples at close and stand-off distances (19 m). Because of its many advantages compared to previously deployed and current in-use methods of elemental analysis (e.g. x-ray fluorescence, APXS), LIBS has potential for application to other planetary bodies. Of particular interest are the Moon and asteroids having very low ambient gas pressures at the surface. Because the laser plasma used by LIBS is sensitive to the surrounding atmosphere, it is important to determine analysis capabilities under these conditions. The results of a study of LIBS capabilities at low pressure is presented here for both in-situ and stand-off analysis.

Experimental: Two experimental set-ups were used. In the first set-up, simulating an in-situ or close-up analysis, samples were maintained in a small chamber. The chamber was connected to an oil-less pump that reduced the pressure to < 0.0001 torr. Gases were flowed through the chamber using a needle valve to maintain a uniform pressure. Laser pulses from a Q-switched Nd:YAG laser (10 ns pulsewidth, 3 Hz, 40 mJ pulse energy, 1064 nm wavelength) were focused on the samples using a 100-mm focal length lens. Plasma light was collected by a fiber optic pointed at the plasma and then transported to one of two detection systems. The first was a spectrograph (Chromex 500IS) and ICCD (intensified CCD) detector combination. The second was an echelle spectrograph and ICCD. The first system provided greater sensitivity compared to the echelle because of its much lower f-number (f/4 vs. f/10). On the other hand, the echelle system provided simultaneous detection of the LIBS spectrum over a wide range (200-800 nm) from each laser plasma compared to the restricted spectral range of 17 nm provided by the Chromex.

The second set-up, shown in Fig. 1, simulated stand-off measurements at 5.3 meters. Nd:YAG laser pulses were directed into a beam expander (x10) and then focused on the samples through a long evacuated tube connected to a sample chamber. Samples (either pressed soil powders or small mineral or rock specimens) were fixed to a large rotatable wheel inside the chamber so different samples could be interrogated sequentially without breaking vacuum.

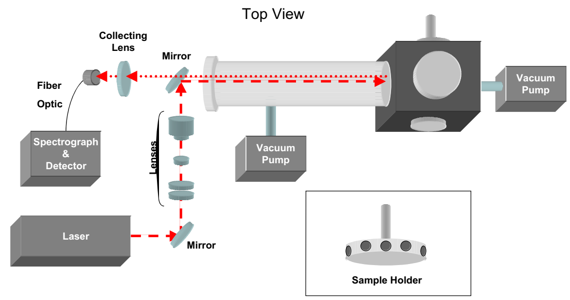

Fig. 1. LIBS apparatus used for measurements at stand-off distances with the sample at pressures down to 0.0003 torr.

Plasma light, collected through the evacuated tube by a 10 cm diameter quartz lens, was focused onto a fiber optic cable. The light was directed into either the echelle spectrograph or one of three compact spectrograph/detector systems (Ocean Optics, HR2000) under evaluation.

Results: A comparison of the visual appearance of plasmas formed on a basalt rock at 7 torr (representa-

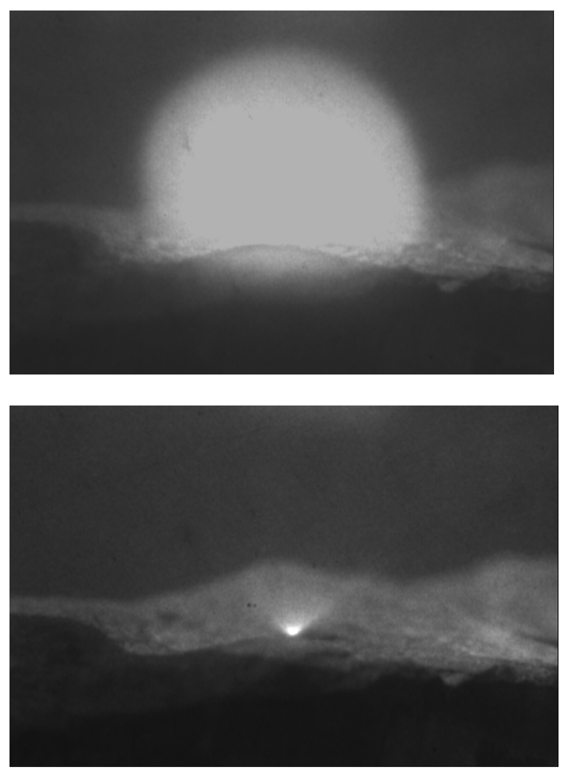

Fig. 2. Comparison of the LIBS plasma at 7 torr (top) and 0.00012 torr (bottom). Width of the image is about 4 cm.

tive of the Mars surface) and at 0.00012 torr (considered here to be representative of the Moon or an asteroid) is presented in Fig. 2. These images were obtained with ICCD gate delay and width settings of td=2 μs, tb=80 ms.

At 7 torr, the plasma appears as a large luminous cloud, much larger than at atmospheric pressure. This is due to the high pressures generated in the plasma [4] and the lower pressure of the surrounding atmosphere that reduces confinement of the plasma to the surface to a lesser extent than at atmospheric pressure. At ambient pressures used here to simulate the Moon, ~0.0003 torr, the plasma appears much weaker in intensity and is confined to a small region near the surface. Here, there is no strong cyclic excitation of material in the plasma near the surface.

Using the first set-up, the pressure dependence of emissions from selected elements was determined. The results are shown in Fig. 3. The pressure range extends from 585 Torr down to 0.00002 torr. The Si and Mg data were acquired from a basalt rock sample while the K data were acquired from a pressed basalt powder (VSMO-13) having greater K concentrations. Data were acquired using the echelle spectrograph with td and tb at 1 μs and 50 μs, respectively. The laser energy was 40 mJ/pulse and 100 laser shots were integrated to produce each spectrum.

As the data show, as the pressure is decreased from atmospheric, emission signals for Si(I), Mg(I) and Mg(II) increase, peak around a pressure of 10 torr and then decrease with decreased pressure. Maximizing of emissions signals at pressures of 10-100 torr was reported previously and was attributed to increased mass of ablated target as the pressure was decreased [1]. At pressures below about 0.003 torr, no further decrease in emissions was observed with decreased pressure, indicating that a steady state regime of ablation-excitation is attained, not affected by a further reduction in pressure. Emissions from other elements behave similarly at lower pressures. The observation of lines at 0.0001 torr and below depends on elemental concentration and the ability of the laser to ablate an adequate amount of the material. Therefore, it appears that at the low pressure characteristic of the Moon (~10^{-9} torr), LIBS should be able to provide elemental analysis at least at close range (<10 cm).

In addition to element emissions, emissions from simple molecules formed in the cooling plasma were also examined along with the dependence of emission decay times on pressure. Spectra from the molecules were observed even at the lowest pressures used here. Also, rates of ablation of 40 mJ laser pulses through

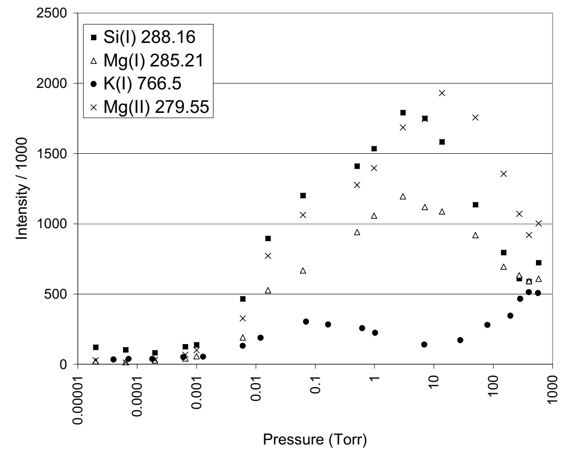

Fig. 3. Dependence of LIBS element signals on ambient pressure.

basalt rock samples was determined at 5.3 meters and the identification of minerals was demonstrated.

Table 1 lists detection limits (DL) for stand-off analysis calculated using calibration curves for elements in eight soil and stream sediment samples. The pressure was 0.0003 torr and the laser energy was 40mJ/pulse. Here td and tb were 700 ns and 50 μs, respectively.

Table 1. Low pressure (0.0003 torr) LIBS detection limits at 5.3 m.

Element/compound	Line (nm)	DL (wt%)
Li	670.77	0.005
K_2O	766.49	0.7
Na_2O	588.99	0.3
Ba	455.40	0.021

The data in Table 1 are comparable to and in some cases better than those obtained at in-situ distances (close range). This is attributed in part to the better reproducibility (lower standard deviation of emission signals) of the spectra at stand-off distances. These and other data to be reported demonstrate the use of LIBS at pressures simulating the Moon and asteroids for stand-off and in-situ detection.

References: [1] Knight A.K. et al. (2000) Appl. Spectrosc. 54, 331-340. [2] Colao F. et al. (2004) Planet. Space Sci. 52, 117-123. [3] Salle B. at al. (2004) Spectrochim. Acta 59B, 1413-1422. [4] Root R.G., "Modeling of Post-Breakdown Phenomena", in *Laser-Induced Plasmas and Applications*, L.R. Radziemski and D.A. Cremers, Eds. (Marcel Dekker, New York, 1989), Chapter 2.