

IN-SITU 1-D AND 2-D MAPPING OF SOIL CORE AND ROCK SAMPLES USING THE LIBS LONG SPARK. K.T. Rodolfa¹, D.A. Cremers¹, and M.H. Ebinger², ¹Advanced Chemical Diagnostics and Instrumentation Group, Los Alamos National Laboratory (MS J565, Los Alamos, NM 87545 USA; cremers_david@lanl.gov), ²Atmospheric, Climate, and Environmental Dynamics Group Los Alamos National Laboratory (MS J495, Los Alamos, NM 87545 USA; mhe@lanl.gov).

Introduction: LIBS is being developed for stand-off interrogation of samples up to 20 m from a lander or rover [1,2]. Stand-off capability is important to access targets not conveniently located for in-situ analysis. On the other hand, in-situ techniques are still important and are being developed for future missions such as MSL. Retrieved samples may consist of loose soils, subsurface soil cores, drilled rock cores, and ice cores. For these sample types, it is possible to employ LIBS analysis and take advantage of LIBS capabilities. These include (1) rapid analysis, (2) good detection sensitivity for many elements, (3) good spatial resolution (3-100 microns), and (4) ability to clean a surface prior to analysis. Using LIBS, it is possible to perform a 1-dimensional analysis, for example, determining element concentrations along a soil core [3], or a 2-dimensional mapping of the sample surface using a unique “long” spark [4].

Two-dimensional sampling has been developed previously by focusing the laser pulses as small spots on the sample and then moving the sample a short distance between sampling locations [5]. Although demonstrated, this method is time consuming, requiring a large number of shots to span even a small region (for 3 micron resolution, an area 600 x 480 microns sampled in \approx 30 min using a 20 Hz laser). For a spacecraft instrument, the ability to more rapidly prepare a 2D elemental spatial map will be desirable. Here we discuss the use of LIBS for sampling along a core in 1D (detection of carbon) and for 2D mapping of a rock face.

Experimental: Core samples were analyzed in the usual way by focusing laser pulses on the core perpendicular to the core axis. The cores used here were up to 1 m in length. The plasma light was collected by a fiber pointed at the plasma (50 mm distance) and then transported to an echelle spectrograph and ICCD for detection.

The imaging portion of the experimental apparatus used here for 2D analysis is shown in Fig. 1 [6]. A Nd:YAG laser operating at 1064 nm produced the laser pulses. Laser light was focused onto the sample with a series of cylindrical lenses as depicted in the figure, producing a spark approximately 1 cm in length on a rock sample. This

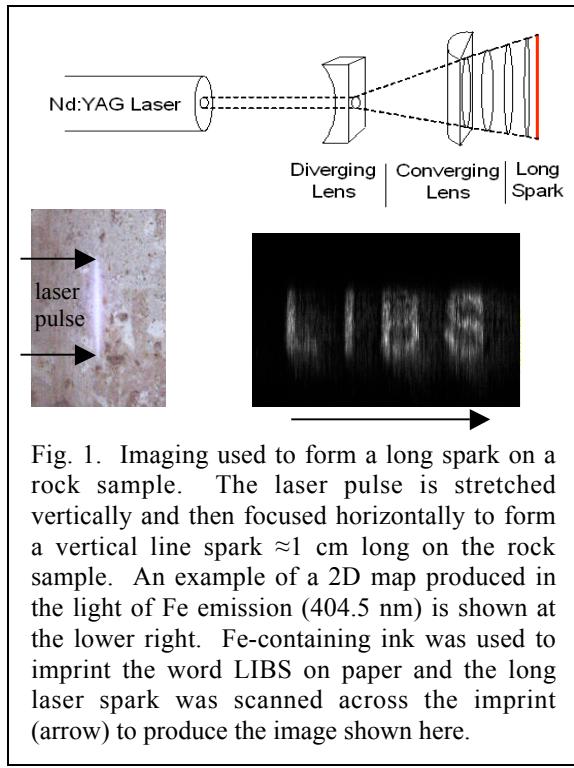


Fig. 1. Imaging used to form a long spark on a rock sample. The laser pulse is stretched vertically and then focused horizontally to form a vertical line spark \approx 1 cm long on the rock sample. An example of a 2D map produced in the light of Fe emission (404.5 nm) is shown at the lower right. Fe-containing ink was used to imprint the word LIBS on paper and the long laser spark was scanned across the imprint (arrow) to produce the image shown here.

so-called long spark interrogates a line, rather than a small spot, at one time on the sample. The rock was translated under the sparks using a motorized translation stage. The combination of data along the spark axis with motorized translation normal to the spark axis allowed the production of three-dimensional maps of element locations across a surface. Light from the spark was collected and focused on the entrance slit of a SPEX 1870 Czerny-Turner spectrometer. The spectrally-resolved light was focused onto an Andor DH534 gated, intensified CCD detector. Spatial information presented at the entrance slit along the long spark was preserved and detected vertically along the ICCD array at the spectrograph focal plane thereby preserving the spatial information.

1D Core Analysis: The results of a mapping of the variation in C signal at 247.8 nm (ratioed to Si at 250.6 nm) is shown in Fig. 2. The detection limit for carbon on soil using LIBS is typically 500 ppm. Each measurement is the average of light from 100 laser pulses at the indicated position of the core. The results show a decrease in C concentration with depth as expected. The resolution of the core depends only

on the degree of translation between sampling locations. Although only carbon is shown in Fig. 2, because the data was acquired using an echelle spectrograph, similar spatial data was obtained

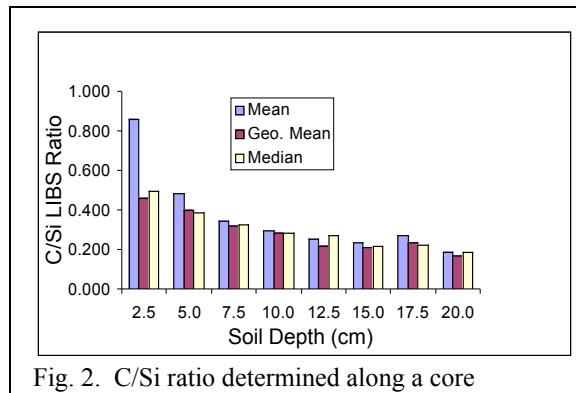
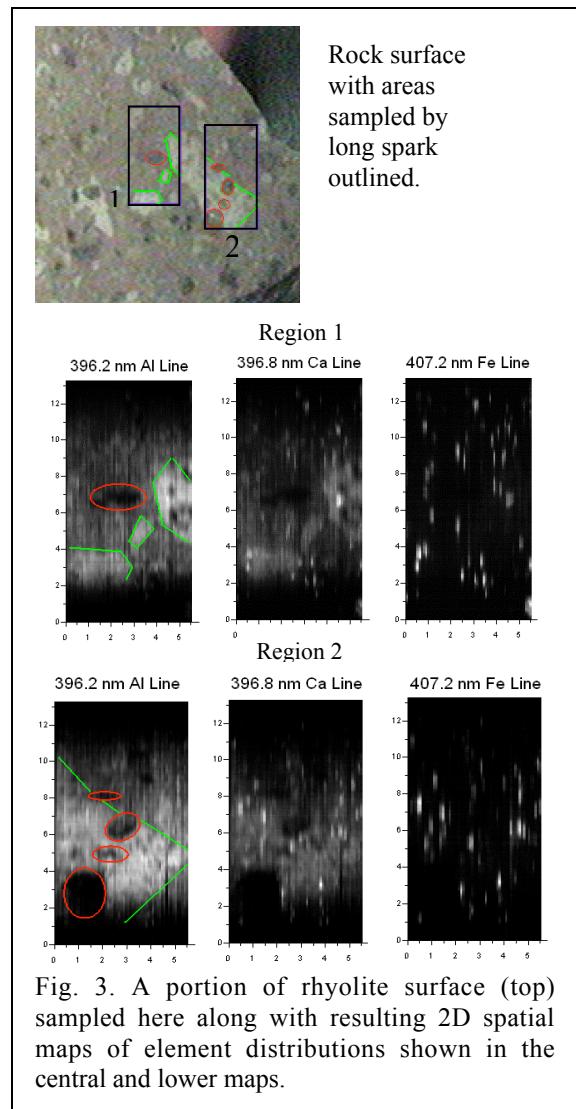


Fig. 2. C/Si ratio determined along a core sample at positions separated by 2.5 cm.



simultaneously for a large number of other elements along the core.

2D Mapping: A visual inspection of the rhyolite rock face shown in Fig. 3 indicates it is composed of three major visually distinct regions – white and colorless spots set in a pink-colored medium. Furthermore, a closer inspection of the rock face reveals a distribution of tiny black spots (which, unfortunately, are difficult to see in Fig. 3). Spectra obtained from conventional LIBS analysis using the pulse focused to a spot, reveal that the white and pink regions are replete with Ca and Al (other spectroscopic work shows that the white regions are slightly enriched in both elements in comparison with the pink regions), while the colorless spots are practically devoid of strong elemental emissions in the region of the spectrum monitored (389.8 to 410.8 nm). Indeed, the colorless regions exhibit low intensities throughout the entire spectrum (200-800 nm using an echelle spectrograph). Compared to the white and pink regions, the tiny black spots indicate relatively high Fe content and somewhat higher Ca.

The regions marked in Fig. 3 were investigated using long-spark multi-elemental analysis in the spectral range of 389.8 nm to 410.8 nm. Data at the Al, Ca, and Fe lines from these scans are shown in the central and lower intensity maps of Fig. 3. All data were obtained simultaneously without making multiple passes over the surface to obtain distributions for different elements. The data from the elemental mapping show excellent agreement with a visual inspection of regions 1 and 2 as well as the spectral data obtained by conventional (spot) LIBS analysis. As noted above, the small black dots are not, unfortunately, visible in Fig. 3, however their presence, as suggested by the iron and calcium maps, can indeed be confirmed by a close visual inspection of the rock surface, even after ablation has occurred.

Conclusions: LIBS can be used to monitor the spatial distribution of elements along a core sample to determine element distribution with position. In addition, using a 2D imaging system, spatial maps can be developed of a rock surface to map out element distributions. Use of the “long” LIBS spark can speed analysis by at least an order of magnitude.

References: [1] Knight A.K. et al. (2000) *Appl. Spectrosc.* 54, 331-340. [2] Wiens R.C. et al. (2002) *J. Geophys. Res.*, 10.1029/2000JE001439. [3] Bolger J.A. (2000) *Appl. Spectrosc.* 54, 181-189. [4] Cremers et al. (1985) *Appl. Spectrosc.* 39, 57-63. [5] Menut D. et al. (2002) *Technical Digest of Laser-Induced Plasma Spectroscopy and Applications Conference* (Orlando, FL, 2002). [6] Rodolfa K.T. et al. (2004) to be published in *Appl. Spectrosc.* April, 2004.