INTEGRATED MICRO-LIBS, RAMAN SPECTROSCOPY, AND MICROSCOPE FOR SPACE EXPLORATION.

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Introduction: Detailed investigation of prepared and unprepared surfaces at the microscopic scale has been used extensively to study the origin and history of geologic samples in terrestrial labs [1] and on Mars [2]. An integrated camera, handlens, and microscope probe is in development for prospecting and science investigations that currently integrates visible reflected light imaging with Raman Spectroscopy, Raman/CHAMP. This instrument images from infinity down to high resolution microscopy, the closer the instrument is placed to a target the higher the resultant image resolution with an associated smaller field-of-view. In the vicinity of peak magnification (~3 micron/pixel), a high resolution laser scan across the microscopic field of view is possible with a <10 micron laser spot for the purpose of analyzing the surface chemistry of particular microscopic features. This instrument provides its own context imaging for progressive high resolution field microscope investigations. Furthermore, the instrument can provide a 3D microscopic surface map built from multiple image scans with slightly different working distances (i.e. image cube) that are subsequently focal-plane merged together to produce a single in-focus image with local elevation coordinates [3]. Combined LIBS and Raman spectroscopy instruments for planetary exploration have been discussed elsewhere [4,5,6], and are considered to have a high potential due to the similarities in the spectroscopic and laser source requirements of LIBS and Raman, and the complementary nature of the LIBS and Raman data sets. LIBS provides elemental information about a sample, while Raman Spectroscopy provides molecular information. Standoff LIBS and Raman Spectroscopy integrated instruments have received the most attention in the space science community. We have investigated LIBS on rock samples at the microscopic (<20 μm spot diameter) scale and with micro-joule laser pulse energy (<200 μJ), which in the LIBS community is referenced as micro-LIBS. We are investigating the potential to incorporate micro-LIBS in the Raman/CHAMP instrument.

Experimental: LIBS experiments were carried out in a low pressure simulated martian atmosphere. A schematic diagram of the experimental apparatus used for LIBS is shown in Figure 1. The laser was focused onto a sample by a custom three element focusing optic with 17 mm working distance and f/2.8. Microscopic images of craters remaining after LIBS plasma generation on hematite samples with 10-20 pulses per spot showed a 15-18 μm diameter. The sample, translation stage, laser delivery optic, and LIBS collection optic were housed in a low pressure chamber. Pressure was varied from 1 torr to 100 torr in a simulated martian atmosphere. The 7 spectrometers span the spectral range of 195 to 970 nm were from an Ocean Optics LIBS 2000+ system. Additional experimental details can be found in [7].

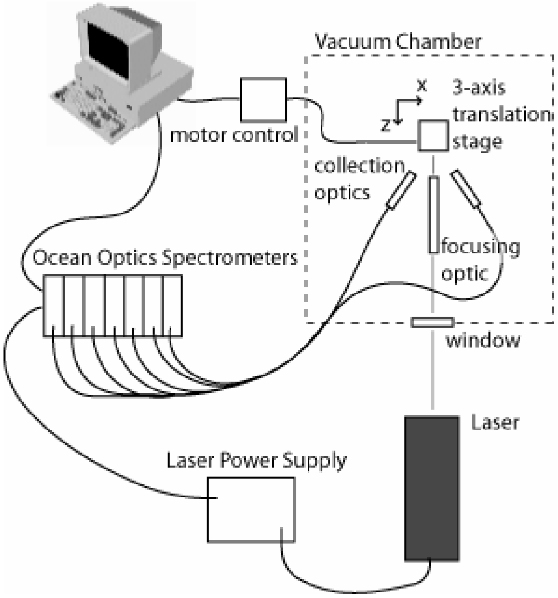

Figure 1: Schematic of micro-LIBS experimental setup.

LIBS plasma emission was collected via seven optical fibers each with a single element optic of 12 mm focal length in 1:1 imaging configuration, arranged in a mount that enabled alignment of the optics to view the same spatial location, custom designed and constructed by Firestar Engineering. The laser focusing optic could be translated axially relative to the collection optics and each LIBS collection fiber optical assembly could be translated axially to optimize laser delivery and collection alignment.

A diode pumped, actively q-switched, intracavity doubled, Nd:YLF laser was used in this study, produced by Crystalaser, model QG-523-800, of Reno, NV. Nd:YLF output is polarized, lasing at 1053nm on the ordinary axis and at 1047nm on the extraordinary axis. The thermal conductivity of Nd:YLF is large and natural birefringence overwhelms thermally induced birefringence eliminating thermal depolarization. Due to these characteristics Nd:YLF lasers are capable of operation over a broad pulse repetition rate range.

Below 1kHz the laser produces approximately 170 µJ per pulse with 10 ns pulse length. Peak pulse power is about 15kW at pulse repetition rates below 1kHz, sufficient to produce >1GW/cm^2 for spots below 50 µm diameter. Peak power decreases to 14 W at the maximum repetition rate of 100kHz. At 100 kHz rep rate the average power of 200mW is quite sufficient for Raman Spectroscopy.

Results: A sample of oolithic hematite from Clinton, NY, was selected for micro-LIBS scans. The hematite sample was prepared by grinding a portion of the surface with 600 grit SiC paper to produce a relatively flat surface. The Nd:YLF laser was operated at 4 Hz, with 150 µJ/pulse delivered to the surface and irradiance was >6 GW/cm^2. In Figure 2 an image of the hematite surface after scanning is shown. The sample surface was positioned in z (depth) such that 10-20 shots per x-y surface location produced plasma as the laser drilled into the surface.

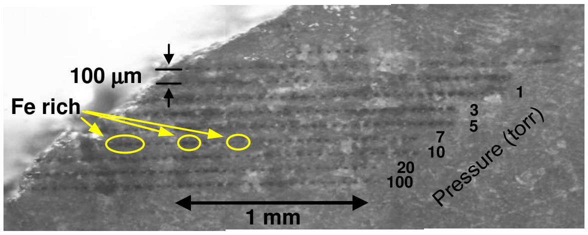

Figure 2: Oolithic hematite sample after micro-LIBS. Horizontal scans correspond to different chamber pressures.

The full averaged spectra at several pressures are shown in Figure 3. Laser scatter was collected along with the plasma emission. Laser pump diode is also observed. Individual LIBS spots were analyzed for relative differences compared to the average spectra at 7 torr in simulated martian atmosphere. In Figure 4 the spectra of several spots are shown that were rich in Fe.

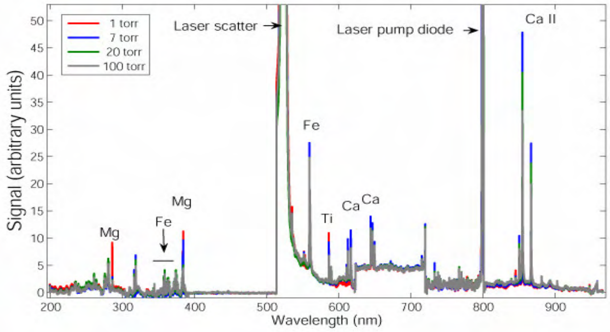

Figure 3: Full spectrum of micro-LIBS on hematite.

The Fe lines increased by about 50% above average, little Mg is seen in the spectra, and Ca II lines are reduced by half relative to the average. This demonstrates the ability to show composition differences using micro-LIBS within a microscope context image.

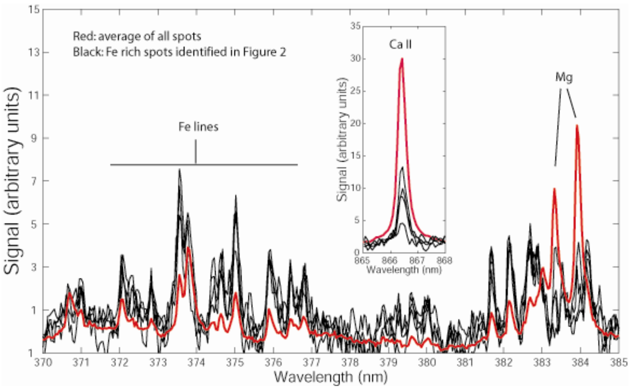

Figure 4: Iron rich spots vs. average of all spots at 7 torr.

Discussion: We have shown the feasibility of micro-LIBS using ~200 µJ (in 10ns pulses) on surfaces of hematite at spots size of < 20 µm. Focus to smaller spots is possible, which will produce hotter plasmas that should result in significantly more signal strength given the strong dependence of LIBS emission signal with plasma temperature [8]. Targeting of the surface must be achieved to depth precision on the order of the spot size, however this functional capability resides with the variable focal length imaging inherent in CHAMP. Futher, the pulse energy can readily be delivered by the CHAMP in its microscopy mode based on Raman/CHAMP results. LIBS laser focus and LIBS emission collection is consistent with the CHAMP optical system, i.e. CHAMP has been shown to be able to focus a green laser to a similar or smaller spot size (diffraction-limited laser spot is 3 micron). In this study >6,000 total shots were delivered to hematite surface with no observalable change in signal strength. In addition, the Nd:YLF laser is a potential option for a combined micro-LIBS and micro-Raman instrument.

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