

**COMBINED REMOTE RAMAN SPECTROSCOPY AND LIBS INSTRUMENTATION FOR MARS ASTROBIOLOGY EXPLORATION.** R. C. Wiens<sup>1</sup>, S. K. Sharma<sup>2</sup>, S. M. Clegg<sup>3</sup>, A. K. Misra<sup>4</sup>, and P. G. Lucey<sup>5</sup>, <sup>1</sup>Los Alamos National Laboratory (LANL; [rwiens@lanl.gov](mailto:rwiens@lanl.gov)), <sup>2</sup>University of Hawaii ([sksharma@soest.hawaii.edu](mailto:sksharma@soest.hawaii.edu)), <sup>3</sup>LANL ([sclegg@lanl.gov](mailto:sclegg@lanl.gov)), <sup>4</sup>U. HI. ([anupam@hawaii.edu](mailto:anupam@hawaii.edu)), <sup>5</sup>U. HI ([lucy@higp.hawaii.edu](mailto:lucy@higp.hawaii.edu))

**Introduction:** Raman spectroscopy and laser-induced breakdown spectroscopy (LIBS) are complementary techniques, both of which use powerful laser pulses to interrogate a sample which can be many meters from the instrument. Raman spectroscopy identifies molecular structure, which can be useful to identify mineral structure or details of organic molecular structure. LIBS, on the other hand, mostly yields elemental compositions, though it can also yield molecular emission in the form of Swan bands. The first LIBS instrument designed for planetary exploration is currently being built as part of the ChemCam instrument on the Mars Science Laboratory (MSL) rover [1,2]. In-situ LIBS and Raman spectroscopy are planned for the ExoMars rover as well. We have been experimenting with instrumentation capable of combined remote Raman spectroscopy and LIBS. Here we describe the techniques, explain why these are highly relevant to astrobiology on Mars, and describe experiments testing the capabilities of a combined instrument.

#### **Why Remote LIBS/Raman Spectroscopy For Astrobiology?**

1) Accessibility. A remote sensing instrument patterned after ChemCam has the greatest accessibility, as it can be used not only for remote distances but also with whatever tools are used for other instruments. For example, drill cores, dirt dug up by wheels, ratted surfaces, and scoop samples can also be interrogated with fine resolution.

Lanza et al. [3] have made a case for exploring gullies with remote-sensing instruments such as ChemCam. Because of the inference that these gullies were made by flowing water, they are of great interest as potential sites of exobiological activity. However, for purposes of planetary protection, gullies have been recommended to be classified as “uncertain” regions [4], and as such, rovers are currently prohibited from traversing gullies. It is a frustrating paradox that the areas of greatest astrobiological interest are off limits from investigation by contact and in-situ instruments. Fortunately, they are not off limits to the instruments discussed here.

2) Habitat characterization. A precursor to finding biological materials themselves is to characterize regions for their potential as habitats. Both LIBS [5] and remote Raman [6] spectroscopy are excellent tools for finding water ice and for finding aqueous-based materials most hospitable to life.

3) Organic elements CHON. Most of the elemental abundance techniques used in planetary exploration are insensitive to the organic elements carbon, nitrogen, oxygen, and hydrogen. LIBS is sensitive to these elements.

**Comparison of LIBS & Raman Spectroscopy:** Beyond the first glance differences noted above, there are many subtle ways in which the techniques can work complementarily.

*Cations vs. anions:* While LIBS and Raman spectroscopy have been viewed as chemical vs. mineralogical/biological techniques, in most rock-forming compounds, Raman spectroscopy tends to identify the anions while LIBS is most sensitive to the cations. A typical example is that Raman spectroscopy immediately identifies carbonates, but must use the precise position of certain peaks to distinguish siderite ( $\text{FeCO}_3$ ) from dolomite ( $\text{MgCa}(\text{CO}_3)_2$ ) from calcite ( $\text{CaCO}_3$ ). A mixture of more than two of these may be mis-identified by Raman spectroscopy. LIBS, on the other hand, readily identifies the cation present, whether Fe, Mg, Ca, or a combination of two or three of these.

*Polymorphs:* Extending the above example, LIBS cannot to first order distinguish calcite ( $\text{CaCO}_3$ ) from aragonite ( $\text{CaCO}_3$ ), while this can readily be done by Raman spectroscopy.

*Organic materials:* Raman spectroscopy can distinguish between various hydrocarbons such as benzene, naphthalene, methane, and their various chemical isomers (e.g., o-, m-, p-xylene, etc.); and different kinds of organic molecules, such as proteins, lipids, amino acids, complex molecules such as pigments, mycosporines, etc [7-9]. LIBS analyses of organic materials have utilized the ratios of emission lines for C, N, O, and H, but they have also used the strengths of molecular emission lines, including relatively strong  $\text{C}_2$  and CN bands. As an example, Morel et al. [10] studied ways to classify and distinguish six different bacteria based on ratios of atomic and molecular emission lines. Similar work has also been done on pollen grains [11]. We have distinguished between glycine ( $\text{C}_2\text{H}_5\text{NO}_2$ ) and lysine ( $\text{C}_6\text{H}_{14}\text{N}_2\text{O}_2$ ) films in simple LIBS experiments in our laboratory.

*Analysis spots:* The LIBS analysis spot is constrained by the laser power density to be small. Producing a laser plasma requires  $\geq 10 \text{ MW/mm}^2$ . With a pulsed laser likely to be flown anytime soon, this con-

strains the analysis spot to always be  $< 1$  mm diameter. Raman spectroscopy does not have such constraints, and our experiments have utilized Raman analysis spot sizes of  $\sim 1$  cm diameter at 10 m. The larger spot size for remote Raman spectroscopy yields better signal/noise.

*Analysis distance:* The same power density requirement limits the distance at which LIBS analyses can be made. The ChemCam LIBS distance requirement is 9 m. Other LIBS experiments have been done to longer distances, up to 45 m [12]. The limiting factor for Raman spectroscopy distances is the  $1/r^2$  nature of the returned signal. Remote Raman spectroscopy measurements have been demonstrated to over half a kilometer [13].

*Removal of dust or weathering layers:* A very significant advantage of LIBS is its ability to remove dust and to profile through weathering layers. Remote Raman spectroscopy benefits from this as well. In one experiment [14], we used a carbonate rock that was covered with basaltic dust such that no Raman signal from the carbonate was observed. The laser was pulsed

with a burst of  $\sim 50$  shots. The shock wave from the expanding plasma removed the dust from a region of  $\sim 1$  cm diameter. Subsequent Raman spectra showed strong carbonate peaks with no sign of interference from the basaltic dust. Another experiment used a calcite sample that was coated with a hematite weathering layer, shown in Fig. 1. Originally only a very weak trace of the  $1085\text{ cm}^{-1}$  line from the symmetric oxygen stretch in carbonate, was visible. The right panel of Fig. 1 shows the LIBS signal from the first 10 laser shots. The spectra show clear calcium peaks, indicating that the laser had punched through the weathering layer within the first ten shots. The final set of ten shots, shown in the bottom right panel, looks similar to the first ten shots. The Raman spectrum shown in the lower left panel was taken last. The clear calcite signal indicates that the weathering layer was sufficiently removed for good Raman analysis to be done on the underlying rock.

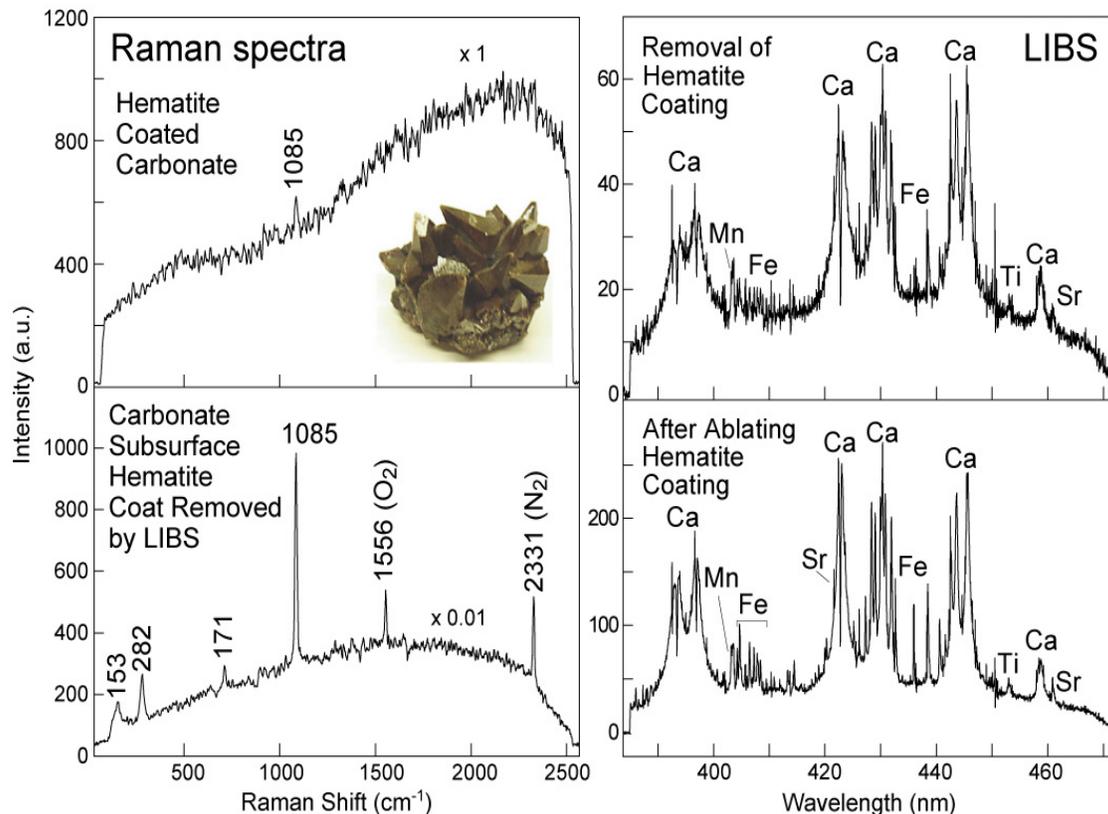


Fig. 1. Remote Raman and LIBS spectra of a hematite-coated calcite sample, taken at 8.6 m distance, showing the action of the LIBS laser resulting in a clean Raman spectrum, lower left. The order in which the LIBS spectra were taken is clockwise, starting with the Raman spectrum in the upper left which shows almost no evidence of carbonate. The Raman spectra were taken with 25 mJ/pulse at 532 nm at 20 Hz for 30 s. The LIBS spectra used 10 pulses each, with a laser power of 45 mJ/pulse. (From [14])

**Simultaneous Remote LIBS and Raman Spectroscopy Measurements:** In most of the experiments over the course of our PIDDP funding Remote Raman and LIBS measurements were made separately using the same apparatus. This is because in many cases different laser powers are needed for the two experiments. Raman emission is excited at lower power densities, and at the higher power densities needed for LIBS, the Raman signals are washed out by the background continuum emission from the LIBS plasma. Two features of our later experimental set-up [14] allowed us to make measurements of LIBS and Raman emission peaks simultaneously. One feature was the use of both the fundamental and frequency doubled Nd:YAG laser light, beam expanded through optics displaying chromatic aberration. This resulted in a tightly focused fundamental beam containing most of the laser power for LIBS with a slightly unfocused 532 nm beam used to excite Raman signals over a larger area. The fact that the LIBS signal exhibits very little white light background at Mars atmospheric pressure helped to minimize the background light. Several experiments were carried out with this set-up.

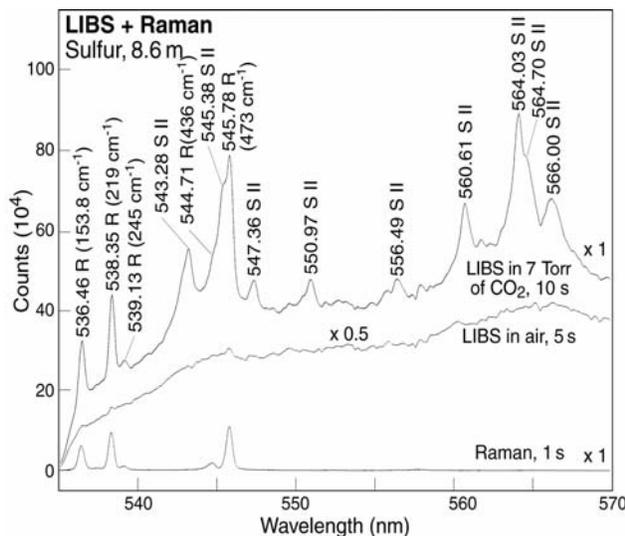


Fig. 2. Simultaneous LIBS (“S II”) and Raman (“R”) emission lines of elemental sulfur shown over a narrow wavelength range, taken at a distance of 8.6 m. (From [14]).

Fig. 2 shows simultaneous LIBS + Raman spectra of elemental sulfur over a small wavelength range obtained in this way. The lower line in the plot shows only a Raman spectrum taken with 5 mJ/pulse at 532 nm. The middle line shows broadband white light emission but no sulfur LIBS emission signal with the

sample in air. The total laser power was 50 mJ/pulse, with 9.3 mJ/pulse at the Raman-exciting 532 nm wavelength. Small bumps in the spectrum are from Raman emission. The top line shows the same measurement made in 7 Torr of CO<sub>2</sub>, simulating the Mars atmosphere. In this case LIBS emission lines of sulfur are easily seen [e.g., 15], along with the Raman emission lines.

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