Combined Remote LIBS and Raman Spectroscopy of Minerals using a Single Laser Source. S. K. Sharma¹, A. K. Misra¹, P. G. Lucey¹, R. C. Wiens² and S. M. Clegg³, ¹Hawaii Institute of Geophysics and Planetology, University of Hawaii, 2525 Correa Rd. HIG, Honolulu, HI 96822, USA (sksharma@soest.hawaii.edu), ²Space Science and Applications, Los Alamos National Laboratory, MS D466, Los Alamos, NM 87544, USA, ³Advanced Diagnostics and Instrumentation, Los Alamos National Laboratory, MS J565, Los Alamos, NM 87544, USA

Introduction: Raman spectroscopy (RS) and Laser-Induced Breakdown spectroscopy (LIBS) are highly complimentary techniques being developed to remotely probe the surface of geological samples. In general, LIBS uses a pulsed 1064-nm laser of high peak power (>1 GW/cm²) for ablating material from the surface of the sample to probe the elemental composition [1, 2]. Raman spectroscopy uses either a CW or a pulsed visible laser of modest average power (100-700 mW/cm²) to identify the molecular finger-prints of the sample from its Raman spectrum [3]. A combined remote Raman and LIBS system suitable for planetary science applications requires a single laser source with no moving parts. We have explored the use of a single pulsed laser operating at dual wavelengths of 1064 nm and 532 nm for exciting both the Raman and LIBS spectra of minerals by adjusting the laser power electronically.

Experimental Setup: Figure 1 is a diagram of the combined LIBS and Raman spectroscopy experimental setup. A detailed description of this combined system can be found elsewhere [4-6]. Both spectrometer systems probed samples placed in air or in a vacuum chamber filled with 7 Torr CO₂ to simulate the surface pressure on Mars.

The combined Raman-LIBS system employed a Surelite Continuum Nd:YAG pulse laser (L) operating at 20 Hz, 7 ns pulse duration, and with a maximum pulse energy up to 130 mJ/pulse. Conversion of the 1064-nm laser beam into a second harmonic at 532-nm was adjusted so as to minimize the power at 532-nm (maximum power 25 mJ/pulse). A plot of total Pₜ(1064 nm + 532 nm) laser pulse energy and that of the 532 nm pulse (Pₜ532) as a function of Q-switch delay time is shown in Fig. 2.

For the combined Raman and LIBS measurements, the signals excited by the Surelite Continuum laser were collected with a 125-mm-diameter reflecting telescope in oblique geometry, coupled directly to a Kaiser F/1.8 HoloSpec transmission-grating spectrograph (TS) through a 100-μm slit after passing through a 532-nm holographic super-notch filter (NF) to remove the reflected and Rayleigh-scattered laser light from the sample (Fig. 1). The detector was a Princeton Instruments intensified CCD detector. The HoloSpec spectrometer measured the Raman spectra from 70 cm⁻¹ to 4500 cm⁻¹ when excited with a 532-nm laser. The grating covered the spectral region from 534 to 699 nm, which was sufficient for identifying some of the major atomic emission lines of measured samples from their LIBS spectra. A 10.8-cm Newtonian reflecting telescope was used to collect some of this optical emission and direct the light into one of three Ocean Optics HR2000 spectrometers (CTS) through a 200-μm fused silica fiber (F) (Fig.1). The three spectrometers were similar to those that will be used for the ChemCam instrument, which includes the LIBS spectrometer selected for the Mars Science Laboratory (MSL) rover. These three spectrometers
record the emission in three regions: 225-320 nm ("UV unit"); 385-460 nm ("VIS unit"); and 500-930 nm ("NIR unit"). The positions of LIBS lines are estimated to be accurate within ± 0.02 nm.

The laser power of the Surelite Continuum Nd:YAG at the sample was electronically controlled by adjusting the Q-switch delay. As the laser pulse power was increased on the sample, we first observed the Raman spectrum of the sample excited by 532 nm beam followed by the LIBS spectrum when the 1064 laser power just reached the laser-breakdown point. At this breakdown point, both the Raman spectrum excited by a larger 532 nm beam and the LIBS spectrum excited within 600 μm diameter circle could be observed simultaneously. Further increase in the laser power created expanding plasma containing the electronically excited ions, atoms, and molecules from the surface of the sample. These electronically excited species emit light at frequencies indicative of the elements present.

Results: Figure 3 shows the combined Raman and LIBS spectra of calcite at 8.6 m in air in the 534-615 nm wavelength range.

At low power (138-μs delay), the upper spectrum in Fig. 3 shows Raman bands of calcites and broad fluorescence due to impurities in the sample. At high laser power (142 μs delay), in the bottom spectrum (Fig. 3) the LIBS signals are enhanced, Raman peaks are still detectable, and the fluorescence background is replaced by white continuum from the plasma. Along with calcium peaks, sodium is detected as the trace impurity element from its D1 and D2 lines at 588.99 and 589.59 nm.

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**References:**


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