

A COMBINED REMOTE LIBS AND RAMAN SPECTROSCOPIC STUDY OF MINERALS. Hugh W. Hubble¹, Manash Ghosh¹, Shiv K. Sharma¹, Keith. A. Horton¹, Paul G. Lucey¹, S. Michael Angel² and Roger C. Wiens³. ¹Hawaii Institute of Geophysics and Planetology, School of Ocean and Earth Science and Technology, University of Hawaii Manoa, 2525 Correa Road, Honolulu, HI 96822. (sksharma@soest.hawaii.edu) ²Department of Chemistry and Biochemistry, University of South Carolina, 631 Sumter Street, Columbia, SC 29208. ³Space and Atmospheric Sciences, NIS-1, MS D466, Los Alamos National Laboratory, Los Alamos, NM 87545.

Introduction: Laser-induced breakdown spectroscopy (LIBS) has been proposed for space exploration [1]. In this paper, we explore the use of LIBS combined with pulsed-laser Raman spectroscopy for mineral analysis at a distance of 10 meters. This concept has been previously proposed [2], but very little laboratory work has been done [3]. We have constructed a remote Raman system utilizing a small pulsed Nd:YAG laser and a 5-inch telescope coupled to a spectrograph with an optical fiber. The performance of this system has been demonstrated previously [4,5]. In this work we have modified the existing system to collect LIBS data, thus obtaining quantitative values for cation composition in our samples. By analyzing the cation information collected in the LIBS experiment alongside the anion information provided by Raman scattering, a more complete image of the mineral's structure and composition can be obtained.

Experimental: The rock forming mineral samples were purchased from Ward's Natural Science Establishment, Inc., Rochester, New York. These samples were used without any polishing or cutting. The calcite sample has large crystals and is from Butte, Montana, USA. The polycrystalline dolomite sample is from Bamble, Norway. The gypsum sample is from Fremont County, Colorado, USA. The magnesite sample is from Riverside County, California, USA. The fosterite sample (Fo 92), a magnesium-rich olivine containing rock, has fine grains and is light greenish color. It is from Jackson County, North Carolina, USA. The olivine sample (Fo 90) came from Puu Mahana, Hawai'i, USA. White coral and pink coral samples were obtained locally.

Laser-induced breakdown spectroscopy. Fig. 1 shows a schematic representation of the experimental setup for the remote LIBS/Raman experiment. A Q-switched, Nd:YAG laser (Quanta-Ray DCR-2, Spectra-Physics, 1064 nm, 20 Hz), operating at ~200 mJ/pulse, was focused on the sample approximately 10 m away creating a plasma spark. A 5-inch telescope (Meade ETX-125 Maksutov-Cassegrain, 127 mm clear aperture, 1.9 m focal length) was focused on the spark. The telescope is placed beside the laser in order to get as close to the 180° back scattering geometry as possible. The telescope is coupled to a ¼ meter spectrometer (Spex 270M) with a multi-mode fused silica optical fiber. A lens collimates the light from the output of the telescope and a 10X microscope objective focuses the

light onto the optical fiber. The light leaving the fiber is collected and collimated by a lens. An objective lens focuses the light at the entrance slit of the spectrometer. The LIBS spectra were recorded with a thermoelectrically cooled, gated and intensified CCD (Princeton Instruments, Inc. I-Max-1024-E). The slit width was 50 µm. Averaged number of accumulations for each spectra was 100. Fig. 2 shows examples of the LIBS spectra produced by this system.

A radiometrically calibrated broadband light source, a Labsphere® integrating sphere, is used to determine the response function of the system by placing the integrating sphere at the sample location, and collecting a spectrum with the identical gain and integration settings used during LIBS measurements. This measurement allows us to calibrate to radiance, the observed signal over the entire optical path. By dividing the sample spectrum by the measured response function, the system response effects are removed and the sample spectrum is calibrated directly in spectral radiance units ($\text{Wm}^{-2}\text{sr}^{-1}\mu\text{m}^{-1}$).

Remote Raman spectroscopy. The experimental setup for our remote pulsed Raman system has been

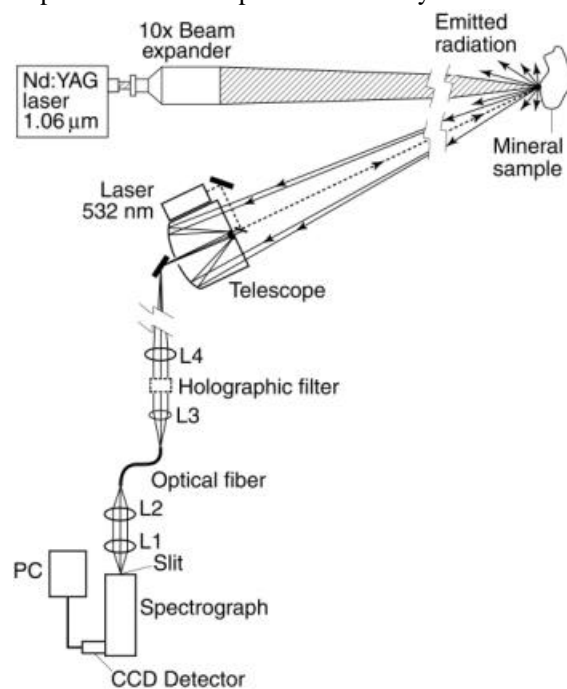


Fig. 1. Schematic representation of the remote LIBS/Raman setup.

described previously [4,5]. It uses a small, frequency doubled Nd:YAG laser source (Model ULTRA CFR, Big Sky Laser, 532 nm, 20 Hz) with the telescope and spectrometer system described above. The holographic notch filter was used to suppress the Rayleigh scattered light from the sample. For recording each of the spectra shown in Fig. 2, the laser power was set to 28 mJ/pulse, the exposure time was 5 sec and the number of accumulations was 10.

Results: Selected LIBS spectra collected in the region around 530 nm (Fig. 2) show a strong Ca-line at 534.94 nm (Fig. 2, calcite). Three strong peaks of Ca are visible in the 526-528 nm region. Five lines are expected in this region, but these lines were not resolved. Also, there is a Ca line at 518.9 nm. Three Mg lines appear at 516.73 nm, 517.26 nm, and 518.36 nm (Fig. 2, magnesite). We chose to evaluate the Mg-data at 517.26 nm, as this line is well resolved.

The dolomite spectrum (Fig. 2, dolomite) is used to adjust for the strength of the individual lines, as the ratio of Ca to Mg in dolomite is 1:1. In this way, we can determine that the ratio of Ca to Mg in our pink coral sample (Fig. 2, pink coral) is 89.3:10.7 mol%. This value of Ca:Mg for pink coral is within $\pm 0.5\%$ to the value of 90.1:9.9 mol% measured by electron microprobe [6]. We did the same experiment using gypsum and white coral, as well as an analysis of the Fe content in magnesium-rich olivine (Fo 90, Fo 92). The Fe content of these minerals determined with remote LIBS is in agreement (within $\pm 0.5\%$) with the electron microprobe analysis of the respective samples.

In the Raman spectra of all four samples a Raman band at $\sim 1085 \text{ cm}^{-1}$ is observed (Fig. 3). This band is very strong in the Raman spectra of calcite, magnesite, and dolomite and is very weak in the spectrum of pink coral. The presence of a 1085 cm^{-1} band in these samples indicates that these mineral contain CO_3^{2-} ions [7]. The strong Raman band at 1130 cm^{-1} in the spectrum of pink coral is characteristic of resonance Raman spectra of the carotenoid pigment [6], and implies biogenic origin of this sample.

The low frequency lattice modes of calcite, magnesite and dolomite, respectively, appear at 281, 329 and 299 cm^{-1} (Fig. 3), and can be used to identify the types of carbonate minerals. The lattice modes are very weak and broad in the spectrum of pink coral because of disorder and the micro-crystalline nature of the biogenic carbonate [6].

The quantitative cation data provided by LIBS, when combined with the unique Raman signature of the anion groups [4], will allow us to remotely identify and characterize the composition and mineralogy of crystals and rocks on planetary surfaces. The remote LIBS and Raman data on selected minerals clearly

demonstrates that development of a combined LIBS and Raman instrument will be very useful for planetary applications.

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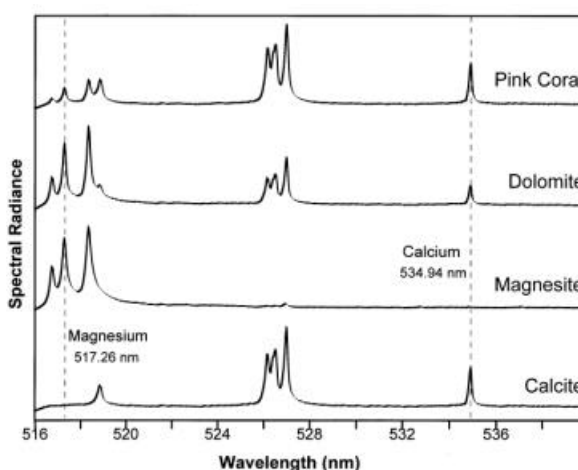


Fig. 2. Portions of LIBS spectra of biogenic (pink coral) and a-biogenic carbonates. Peaks at 517.3 nm and 534.9 nm are used to determine Mg and Ca concentrations, respectively.

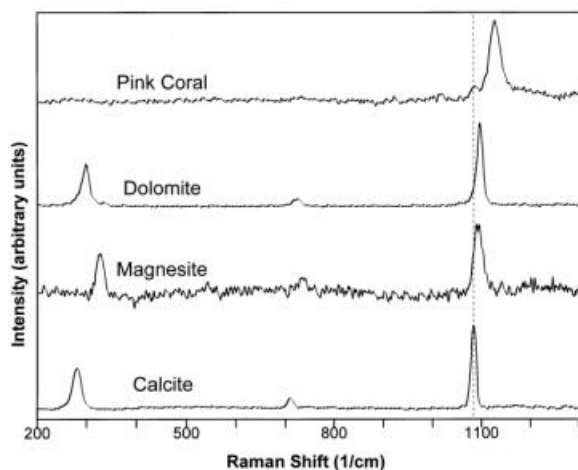


Fig. 3. Raman spectra of biogenic (pink coral) and a-biogenic carbonates. Raman lines near 1085 cm^{-1} are characteristic of the CO_3^{2-} .