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LIBS – RAMAN RESEARCH FACILITY AT LOS ALAMOS NATIONAL LABORATORY. S.M. Clegg[1], R.C. Wiens[1], D.M. Delapp[1], R.E. McInroy[1], and S. Maurice[2], [1]Los Alamos National Laboratory, Los Alamos, NM, sclegg@lanl.gov, rwiens@lanl.gov, [2]Institut de Recherches en Astrophysique et Planétologie, Toulouse, France.

Introduction: Los Alamos National Laboratory has a research facility dedicated to the development of Laser-Induced Breakdown Spectroscopy (LIBS), Raman, and fluorescence spectroscopy instrumentation, data analysis and fundamental scientific investigations. The facility includes a functional replica of the ChemCam instrument on the Mars Science Laboratory (MSL) rover, capable of LIBS analyses to 7 meters distance.[1,2] The SuperCam instrument selected for the Mars 2020 (M2020) rover includes an integrated Raman, LIBS, Time-Resolved Fluorescence (TRF) and Visible and Infrared (VISIR) Reflectance spectroscopy. A functional replica of the SuperCam instrument is intended to be added to this laboratory. Finally, a R&D LIBS, Raman and TRF test stand is available in the laboratory that was used to define many of the ChemCam and SuperCam instrument requirements.

LIBS involves focusing a pulsed laser onto a tight spot on a sample surface. The laser ablates material from the surface, generating an expanding plasma containing electronically excited atoms, ions and small molecules. The excited species emit light at wavelengths diagnostic of the species present in the sample as they relax to lower electronic states. In Stand-off LIBS, some of this emission is collected with a telescope and directed into a spectrometer suite. Raman spectroscopy involves lower-power-density stimulation resulting in weak emission of the surface molecules. TRF involves analyses of the time spectrum of fluorescence emitted from a stimulated surface.

The ChemCam and SuperCam instruments use three separate spectrometers to cover most of the 240 – 860 nm spectral range. They use a similar Nd:YAG-like laser (14 mJ/pulse on target) and 110 mm telescope for the LIBS, while SuperCam adds a frequency-doubled 532 nm beam for Raman spectroscopy and TRF. The UV (245 - 340 nm) and Violet (380 - 470 nm) reflection spectrometers are nearly identical for both instruments. SuperCam uses a transmission spectrometer to cover VNIR (535 – 860 nm) LIBS, Raman (150 – 4400 cm^{-1}), and TRF analyses [3]. Distance capabilities are to 7 m for LIBS (both instruments), to ~12 m for Raman and TRF (SuperCam), and to infinity for imaging (both instruments) and VISIR reflectance spectroscopy (400 – 900 nm, 1.3 – 2.6 µm for SuperCam).

ChemCam Test Stand: The ChemCam testbed includes both the LIBS elemental analysis capability as well as the black and white remote micro-imager (RMI). A similar ChemCam testbed is in use in Toulouse, France. LIBS is sensitive to the atmospheric pressure above the samples. LIBS performance is optimized between 10 and 100 Torr and is ideal for Mars surface investgations. In order to simulate the Mars surface conditions, samples are placed in a vacuum chamber and filled with 7 Torr CO_2 or Mars gas (including several percent argon and nitrogen). The vacuum chamber is placed on a rail system that enables one to move the chamber from 1.5 to 7 m from the ChemCam mast unit to simulate the full range of ChemCam standoff capabilities.

The ChemCam science team has developed a data analysis pipeline that enables direct comparisons with the ChemCam instrument on Mars.[4] The data analysis methods include background subtraction, noise removal, continuum removal, spectral calibration and resampling, and an instrument response function. Similar methodology is under development for the other test stands.

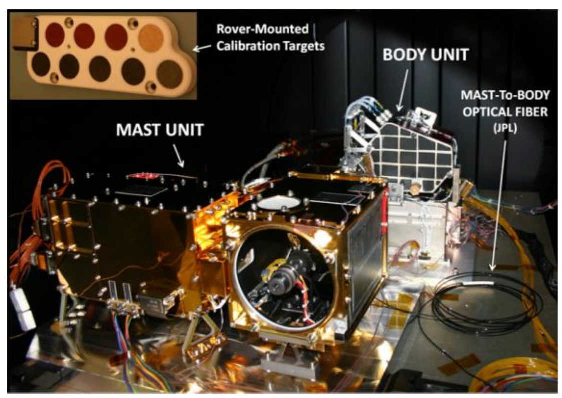

Figure 1. Image of the ChemCam mast and body units. For scale, the aperture of the telescope is 110 mm diameter.

R&D Test Stand: The R&D test stand includes a Spectra Physics Nd:YAG laser that is capable of more than 100 mJ per 8ns pulse at 1064 nm.[5,6] The laser is directed through a frequency doubling unit to produce more than 20 mJ/pulse at 532 nm. These two beams are separated such that the 1064 and 532 nm beams simulate ChemCam and SuperCam performance. The 1064 nm beam is directed through a 10x beam expander to focus the laser on sample up to 12 m away for remote LIBS analysis. The 532 nm laser is expanded to ~1 cm diameter and is collimated out to 12 m to simulate the SuperCam Raman and TRF spectroscopy modes.

Some of the Raman and LIBS emission is collected with a 89 mm Questar telescope and directed into an optical fiber. The fiber enables one to use a wide variety of spectrometers including a new advanced spectrometer suite based on the ChemCam and SuperCam architectures. The prototype transmission spectrometer capable of detecting both the Raman spectra excited at 532 nm and LIBS in the VNIR region (535 – 860 nm) is a relatively accurate simulation of the SuperCam transmission spectrometer. The test stand also includes UV and Violet spectrometers similar to ChemCam except the ChemCam CCD detectors have been replaced with miniature intensified CCDs. This advanced spectrometer suite was designed to work under the more challenging environments such as the Venus surface.

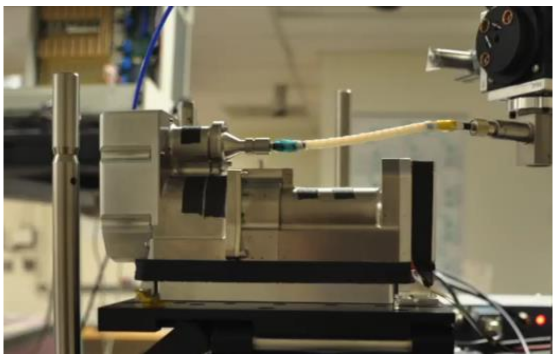

Figure 2. The propotype transmission spectrometer. The spectrometer is 15 cm in length.

SuperCam Test Stand: We intend to add a replica of the SuperCam instrument to this facility in the future. In the meantime, we can simulate the SuperCam LIBS, Raman, TRF and part of the VISIR reflectance spectroscopy with the ChemCam and R&D test stands. This involves using the ChemCam UV and Violet spectrometers to record part of the LIBS spectrum. The LIBS VNIR region, the Raman spectrum, and the TRF spectrum is recorded with the prototype transmission spectrometer.

Samples: The ChemCam test stand has been used to recalibrate ChemCam over the last two years. This effort involed the collection of more than 500 geologic standards that provide a better representation of the diverse geology observed by MSL in Gale Crater. The standards supported not only the major-element calibration, but also specialized calibrations for trace elements. We are also developing a mineralogical library to support future SuperCam investigations. Of course, facility users are also invited to bring their own samples and use the facility prepare samples as necessary.

Sample Chambers: LIBS has been demonstrated to perform accurate elemental analysis under the high Venus surface pressures [6] and in the vacuum of the Lunar surface and on asteroids.[7] Raman analysis has been shown to be completely insensitive to the atmospheric conditions and is insignificantly sensitive to Venus surface temperature (~740 K).

LANL has recently purchased a high pressure and temperature chamber designed to simulate exteme environmental conditions like the surface of Venus. This chamber is on a cart and can be integrated into the R&D test stand discussed above for LIBS, Raman and TRF investigation under Venus conditions.

Another vacuum chamber that is capable of 10^{-7} Torr pressures has been used to simulate the low pressures conditions on the Lunar and asteroid surfaces. This chamber can also be integrated into the R&D test stand for LIBS, Raman and TRF analysis.

Summary: The LANL LIBS – Raman facility has the hardware required to accurately simulate ChemCam and SuperCam geochemical and mineralogical investigations under Mars conditions. The facility also includes the pressure and vacuum chambers required to simulate the Venus, Lunar and asteroid surface conditions for LIBS, Raman, and TRF experiments.

References: [1] Maurice et al. (2012) *Space Science Reviews*, *170*, 95-166. [2] Wiens et al. (2012) *Space Science Reviews*, *170*, 167-227. [3] Wiens et al. (2015) this meeting. [4]Wiens et al., (2013) *Spectrochimica Acta B*, *82*, 1-27. [5] Clegg et al. (2009) *Spectrochimica Acta Part B, 64,* 79-88. [6] Clegg et al. (2014) *Applied spectroscopy*, *68,* 925-36 [7] Lasue et al. (2012) *Journal of Geophysical Research: Planets, 117(E1).*

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