Standoff LIBS and Raman Spectroscopy under Venus Conditions. J. Lambert[1], J. Morookian[1], T. Roberts[1], J. Polk[1], S. Smrekar[1], S. M. Clegg[2], R. C. Wiens[2], M. D. Dyar[3], A. Treiman[4]. [1]Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Dr., Pasadena CA, 91109, james.l.lambert@jpl.nasa.gov, johnmichael.morookian@jpl.nasa.gov, william.t.roberts@jpl.nasa.gov, j.e.polk@jpl.nasa.gov, ssmrekar@jpl.nasa.gov, [2]Los Alamos National Laboratory, P.O. Box 1663 MS J565, Los Alamos, NM 87545, sclegg@lanl.gov, rwiens@lanl.gov, [3]Dept. of Astronomy, Mt. Holyoke College, South Hadley, MA 01075, mdyar@mtholyoke.edu, [4]Lunar and Planetary Institute, 3600 Bay Area Blvd., Houston TX 77058, treiman@lpi.usra.edu.

Introduction: A flight instrument based on a LIBS/Raman architecture is envisioned that quantitatively determines elemental and mineral composition of the Venusian surface by targeting the sample with a laser and spectroscopically analyzing the light collected via a sapphire viewport within a thermally insulated lander. The advantage with this approach is that it can be implemented with no sample handling and the instrument itself is completely shielded from the harsh Venus environment. With the appropriate calibrations models LIBS and Raman can potentially be used to quantiatively measure elemental and mineral composition of geologic samples on Venus. Implicit in this ultimate goal is the need to acquire spectra with high SNR's in the Venus environment over standoff distances required to target samples in the immediate vicinity of a landed spacecraft. Accordingly, we have developed a testbed to demonstrate that Laser Induced Breakdown Spectroscopy (LIBS) and Raman Spectroscopy can be used to acquire high quality spectra of rocks and minerals across standoff distances of up to 1.5m at Venus surface temperature and pressure (VTP) (i.e. 733K/92bar) in a simulated Venus atmosphere (96.5% CO_2/ 3.5% N_2).

Venus Optical Testbed (VOT): The Raman/LIBS testbed (Figure 1A) consists of a 1.6m long pressure vessel within a 4-zone furnace, a gas manifold with gas cylinders allowing the vessel to be filled with a simulated Venus atmosphere, LIBS and Raman spectrometers, and a Nd:YAG laser. The LIBS and Raman system utilize the fundamental (1064nm) and 2nd harmonic (532nm) wavelengths of a Nd:YAG laser, respectively. An optical attenuator allows testing over the 0.2 – 100mJ/pulse energy range. The vessel/furnace assembly can operate under full Venus conditions at 92bar and 733K. Optical access to one end of the chamber is provided through a 10cm diameter, 2.3cm thick sapphire window, diffusion-bonded into a titanium flange. The sapphire used is chromium and iron free (water-white) in order to prevent intrinsic fluorescence during Raman investigations. The c-axis of the window is perpendicular to the face of the window to minimize birefringence effects. An Andor f/4 Czerny-Turner spectrometer with a Gen II iCCD was fiber coupled to a Questar Mark III QM-1 Maksutov-Cassegrain catadioptric reflecting telescope with an entrance aperture of 89mm, which allows collection of LIBS spectra (240-800nm) of samples placed 10cm to 1.5m from the sapphire window of the chamber. A flange-based holder was developed for positioning samples in the center of the vessels optical axis (Figure 1B). For Raman testing, a Holospec f/1.8 Kaiser spectrometer with a Gen III iCCD was fiber coupled to the Questar telescope and is used to collect Raman spectra over 2000cm^{-1} using a single-plex holographic grating.

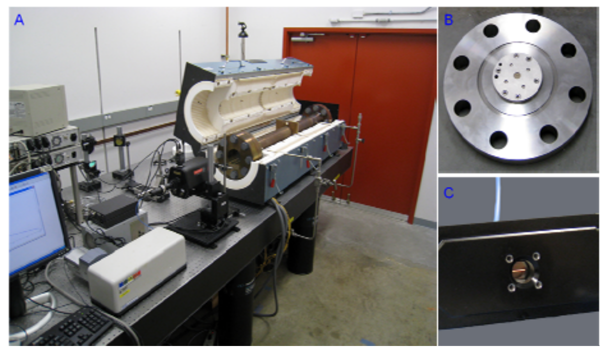

Figure 1: (A) Venus Optical Testbed, (B) Sample holder with end flange, (C) "Circle-to-Line" Fiber-Optic Bundle Assembly

LIBS under Venus Conditions: During our early experiments, beam refraction and temporal wander caused the LIBS signal collected to be weak since the image of plasma plume in the focal plane of the collection telescope frequently moved from the center of the field, sometimes by millimeters. Similar plume shapes were observed at LANL, where tests were also performed under high pressure and temperature (92bar and 423K) in supercritical CO_2[1]. However, beam wander appeared to settle as the system approached equilibrium.

In order for us to maximize the light collected under VTP without loss of resolution, we used a fiber-optic circular-to-line converter in order to collect light from a large area (1mm) in the center of the focal plane (Figure 1C). This approach would help mitigate beam wander issues if they arose. Light from a circular bundle of 37 fibers transferred light collected from the back focal plane of the telescope to the spectrometer in the form of a linear array of the 100 micron diameter core fibers, which served as the instrument's slit. This approach helped capture of the LIBS emission light from the plasma plume while maintaining high spectral resolution. An automated stitch-and-glue approach was used to step the spectrometer across the full 240-800nm free spectral range in 12 discreet bands using a 1200lines/mm grating blazed at 300nm. Using this approach, we were able to collect high quality LIBS spectra at VTP.

One Venus geologic analog made available to us was an alkaline basalt[2]. This sample, (TAP04), is an olivine minette originally mined from the Tapalpa volcanic fields in Mexico. All of the spectral lines for the major and some of the minor elements of interest can be seen in the TAP-04 LIBS spectra (Figure 2). Attenuation and pressure broadening at VTP observed with the TAP04 sample were consistent with LIBS spectra of a basaltic rock previously taken at LANL at Venus pressure (93bar) in N_2 at room temperature by Cremers[3].

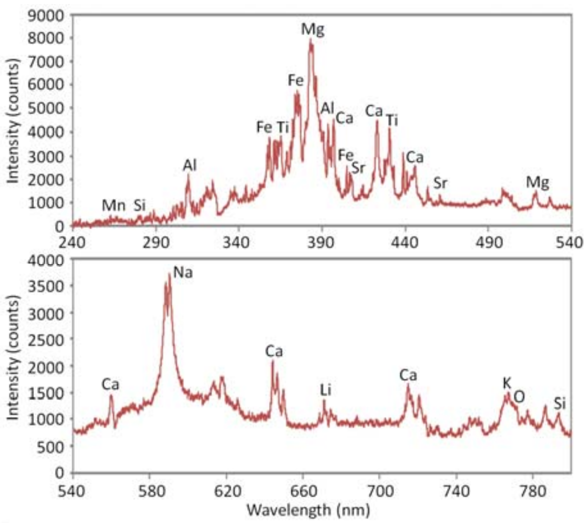

Figure 2: LIBS spectrum of an alkaline basalt sample under Venus conditions

Raman under Venus Conditions: We prepared powdered mineral samples that were pressed into flat cylindrical pellets to provide a flat surface onto which to focus the Raman excitation beam in order to mitigate beam wandering issues. A sample holder held the pellet at the end of the Venus chamber parallel to the sapphire entrance window. Co-added (1000) Raman spectra at STP and VTP were acquired from olivine powder (Figure 3). The powder consisted of a 50-50 mixture of olivine minerals obtained from Arizona and Tanzania. Interference from ambient light and blackbody radiation were not observed. Time-gating of the iCCD all but eliminated their contribution to the spectrum. The spectral features of this particular sample indicated that it was prominently composed of forsterite (Mg_2SiO_4) rather than fayalite (Fe_2SiO_4) because of the prominent peaks at 824cm^{-1} and 856cm^{-1} [4]. Raman peaks present at 1286cm^{-1} and 1389cm^{-1} represented a resonant Fermi diad of supercritical CO_2. Raman peaks at 1265cm^{-1} and 1408cm^{-1} are "hot bands" which increased in height with temperature. The position and peak area ratios of these lines can be used to measure the temperature, density, phase, and isotopic ratios of CO_2[5][6].

Standoff Raman spectra observed were much weaker than the LIBS spectra at both STP and VTP. This was expected since only one photon in 10^9 is Raman scattered. Intensified CCD's mitigate this difficulty by providing gain as well as time-gating capability. To study the effects, we acquired single and co-added sets Raman spectra under Venus conditions using a variety of image intensifier gain and gate-width settings.

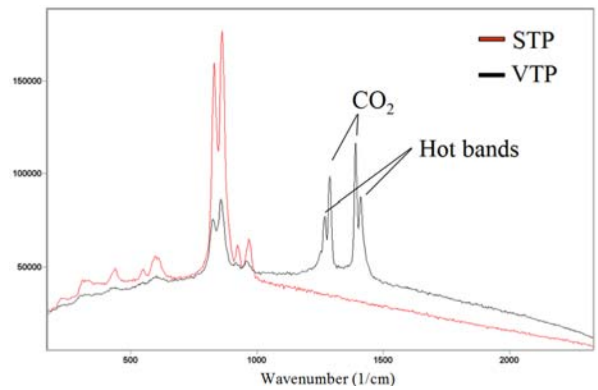

Figure 3: Raman spectra of Olivine acquired under lab ambient (STP) and Venus (VTP) conditions

Summary: For the first time, we have shown that LIBS and Raman spectra can indeed be acquired with reasonable SNR under Venus temperature and pressure conditions in a simulated Venusian atmosphere. Spectral emission peaks corresponding to major and minor elements are easily seen using pulse energies <100mJ for LIBS and <20mJ for Raman across pathlengths (1.5m) commensurate with pathlength requirements envisioned for in-situ exploration with a Venus lander.

References: [1] Clegg, S. et al. (2009) *Venus Geochemistry: Progress, Prospects, and New Missions*, Abstr. # 2013. [2] Basilevsky, A. et al. (2007) *Planet. Space Sci.*, 55**,** 2077-2011. [3] Cremers D. and Radziemski, L. (2006) *Handbook of Laser Induced Breakdown Spectroscopy*, John Wiley and Sons, 214-226. [4] Kolesov B. and Tanskaya, J. (1996) *Mater. Res. Bull.*, *31*, 1035-1044. [5] Arakawa, M. et al., (2008) *Chem. Letts.*, *37*,. 280-281. [6] Arakawa, M. (2007) *Appl. Spectros.*, *61*, 701-705. [7] Bai, Y. (2008) *SPIE Conference on Astronomical Instrumentation*, Marseille, France, 2008.