VENUS GEOCHEMICAL ANALYSIS BY REMOTE RAMAN – LASER INDUCED BREAKDOWN SPECTROSCOPY (Raman-LIBS). S. K. Sharma[1], A. K. Misra[1], S. M. Clegg[2], J. E. Barefield[2], R. C. Wiens[2], C. R. Quick[2], M. D. Dyar[3], M. C. McCanta[4], and L. Elkins-Tanton[5], [1]Hawaii Institute of Geophysics and Planetology, University of Hawaii, 2525 Correa Rd., Honolulu, HI, 96822, sksharma@soest.hawaii.edu, anupam@hawaii.edu. [2]Los Alamos National Laboratory, P.O. Box 1663 MS J565, Los Alamos, NM 87545, sclegg@lanl.gov, jbarefield@lanl.gov, rwiens@lanl.gov, quick@lanl.gov, [3]Dept. of Astronomy, Mt. Holyoke College, South Hadley, MA 01075, mdyar@mtholyoke.edu. [4]Dept. of Geology, Tufts University, Lane Hall, Medford, MA 02155, molly.mccanta@tufts.edu, [5]Massachusetts Institute of Technology, Dept. of Earth, Atmospheric and Planetary Sciences, Cambridge MA, 02139, ltelkins@mit.edu.

Introduction: The extreme Venus surface temperature (740K) and atmospheric pressure (93 atm) creates a challenging environment for future lander missions. The scientific investigations capable of Venus geochemical observations must be completed within several hours of the landing before the lander will be overcome by the harsh atmosphere. A combined remote Raman – LIBS (Laser Induced Breakdown Spectroscopy) instrument is capable of accomplishing the geochemical science goals without the risks associated with collecting samples and bringing them into the lander. Wiens et al. [1] and Sharma et al. [2] have demonstrated that both analytical techniques can be integrated into a single instrument capable of planetary missions. The goal of this effort is to demonstrate that remote Raman – LIBS spectra can be acquired under Venus conditions to yield quantitative geochemistry on Venus-analog rocks.

Experimental: The LIBS experiments involve focusing a Nd:YAG laser (1064nm, 10Hz, 50mJ/pulse) onto the surface of the sample. 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 wavelenghths characteristic of the species present in the sample as they relax to lower electronic states. Some of this emission is collected with a telescope and directed into a solarization resistant fiber connected to a dispersive spectrometer. The samples are placed 1.5m from the telescope in a cell filled with 93 atm of supercritical CO_2 at 423K, a temperature much lower than the 740K Venus surface temperature.

The Raman experiments employed a Nd:YAG pulse laser operating at 20 Hz and with a maximum pulse energy of 15mJ/pulse at 532nm. Two separate Raman experiments will be described in the paper. The first set of experiments involved probing samples as a function of temperature ranging from 300 – 900K and 1 atm. These experiments involve a 5x beam expander to focus the 532 nm laser beams onto the sample at 9 m from the beam expander. The second set of experiments involved placing the samples in the same pressure cell used for the LIBS experiments and probing the samples at 1100 psi and 150°C. The samples were placed 1.5m from the collection optics. These experiments also involved a 532nm probe laser and the spectra were collected with a 1-10 sec integration time.

Sample Selection: Our knowledge of the surface composition of Venus is limited. The most complete data available come from Soviet Venera and VEGA landers. Data from all landers suggest a surface composition that is primarily basaltic [3], although care must be taken when interpreting the data due to the imprecise data, which result in large error bars.

The majority of the sampled material falls in the tholeiitic basalt region with some potentially more calc-alkaline material. However, rocks at both the Venera 8 and 13 landing sites exhibited very high K_2O contents (~4% K_2O), consistent with a shoshonite classification. Due to these observed compositional differences and with the recognition of the imprecise nature of the current data, a range of igneous rock types has been chosen for study. Emphasis is placed on basaltic materials based on the Venera and Vega data.

Table 1. Samples Studied

Sample	Rock Type	Source
TAP-04	olivine minette	[4]
BHVO-2	Hawaiian basalt	USGS
BCR-1	Columbia river basalt	USGS
GBW-07105	Olivine basalt	NRCCRM, China
GUW BM	Basalt	Brammer
JA-1	Japan andesite	GS Japan
SARM-40	Carbonatite	Mintek
GBW-07103	granite	NRCCRM, China
KV04-17	Kauai volcanics	M. Rhodes
KVO4-25	Kauai volcanics	M. Rhodes
Liw Liw creek	Phillipines shoshonite	P. Hollings

Results and Discussion: *LIBS Geochemical Analysis:* LIBS is fundamentally a geochemical analysis tool sensitive to the elemental composition of the sample. The challenge associated with LIBS geochemical analysis under Venus surface conditions involves overcoming the high surface atmospheric pressure and generating the plasma. The collisions between the expanding plasma and the supercritical CO_2 result in the deactivation of electronic states (lower total signal intensity) as well as the appearance of emission lines not typically observed under terrestrial conditions. The resulting spectra are much more spectrally complex (Fig. 1) but many of the typically diagnostic peaks are still observed.

Raman Mineralogical Analysis: Raman spectroscopy is fundamentally sensitive to the molecular signatures present from the sample. Fig. 2 shows the spectrum of olivine in dunite at 303K, 718K, and 878K. The challenge to probing samples with Raman spectroscopy under Venus surface conditions is associated with the surface temperature (740K) and the associated blackbody radiation. The spectra depicted in Fig. 2 demonstrate that most of the Raman spectral features are observed with a properly gated spectrometer and a pulsed laser.

Raman spectra were also collected under supercritical CO_2. Fig. 3 contains the Raman spectra of the same olivine sample under various temperatures and pressures. Inspection of the spectra in Fig. 3 demonstrates that the presence of high pressure CO_2 does not affect the resulting Raman spectra. Note that the baseline observed in Fig. 3 is due to the fluorescence from the sapphire window and not due to the sample. All of the samples probed demonstrated the same spectral quality.

Optical Transmission through Venus Atmosphere. Directing and focusing the laser from a cool Venus lander through a window and into the targeted sample was certainly a concern. Fig. 4 contains the images of the laser plasma generated with the LIBS laser focused to ~250μm diameter. The left image is the plasma (saturated intensity) under terrestrial conditions and the right image is the plasma under 93atm supercritical CO_2 at 423K. The image of the plasma is clearly distorted by the presence of the CO_2 but the peak intensity has not moved. The distortion could be due to the pressure on the window or the orientation of the sample and is under investigation.

References: [1] Wiens R.C., et al. (2005) *Spectrochim. Acta A* **61**, 2324-2334 [2] Sharma, S. K. *et al.* (2007) *Spectrochim. Acta A*, **68** , 1036-1045 (2007); [3] Barsukov VL (1992) Venusian Igneous Rocks. In Venus Geology, Geochemistry, and Geophysics (eds. VL Barsukov, AT Basilevsky, VP Volkov, and VW Zharkov). Univ. Arizona Press, pp. 165-176. [4] Righter K. and Rosas-Elguera J. (2001) *J. Petrol.*, **42**, 2333-2361.

Acknowledgments: We are grateful to Allan Treiman and Kevin Righter for sample selection discussions and to Kevin Righter, Michael Rhodes, Mac Rutherford, and Peter Hollings for providing samples.

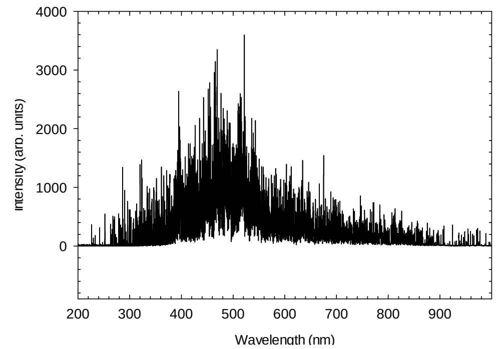

Figure 1. LIBS spectrum of TAP-04.

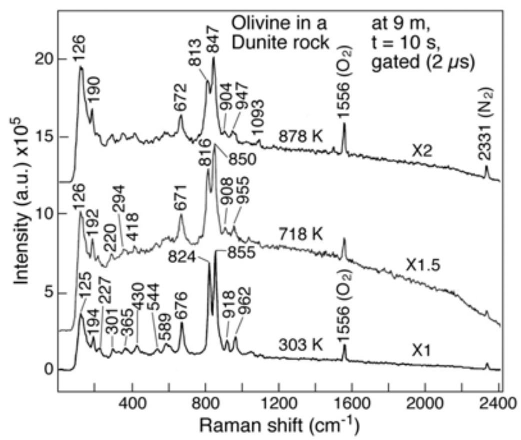

Figure 2. Raman spectra of olivine in dunite.

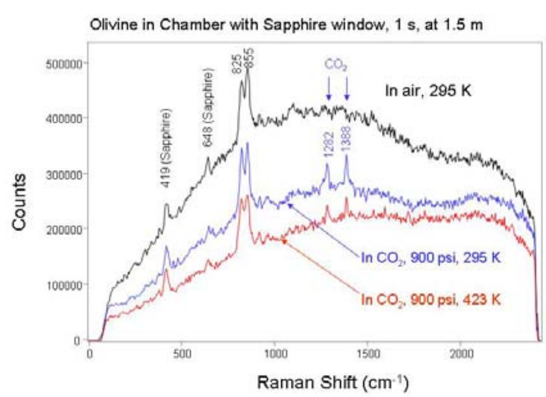

Figure 3. Raman spectra of olivine in the high pressure cell.

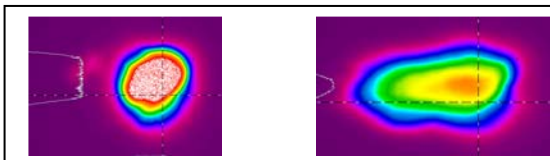

Figure 4. Image of the LIBS plasma generated in the supercritical CO_2 atmosphere.