VENUS GEOCHEMICAL ANALYSIS BY REMOTE RAMAN – LASER INDUCED BREAKDOWN SPECTROSCOPY (Raman-LIBS).

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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 one can integrate both analytical techniques into a single instrument capable of planetary missions. The goal of this abstract is to demonstrate that remote Raman – LIBS spectra can be acquired under Venus consitions 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 diagnostic 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 1.67m from the telescope in a cell filled with 93atm 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 35mJ/pulse at 532nm. A 5x beam expander was used to focus the 532 nm laser beams onto the sample at 9 m from the beam expander.

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 their imprecise nature resulting in large error bars.

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

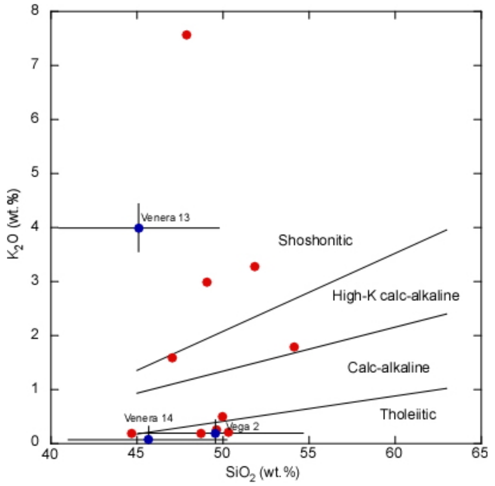

Figure 1. Comparison of Venus compositional data (blue [3]) with terrestrial standard samples (red). SARM-40 (carbonatite: 3.08 wt.% SiO_2, 0 wt.% K_2O), GBW-07103 (granite: 72.83 wt.% SiO_2, 5.01 wt.% K_2O), and JA-1 (andesite: 64.06 wt.% SiO_2, 0.78 wt.% K_2O) are not included.

The majority of the sampled material falls in the tholeiitic basalt region on an SiO_2-K_2O plot (Fig. 1), 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.

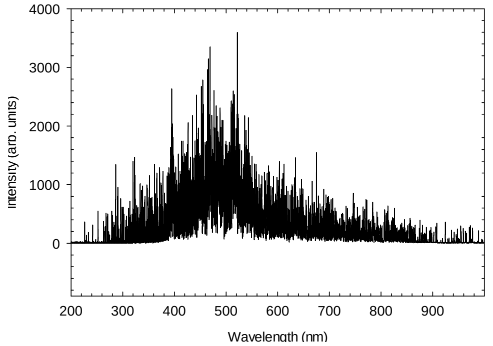

Figure 2. LIBS spectrum of TAP-04.

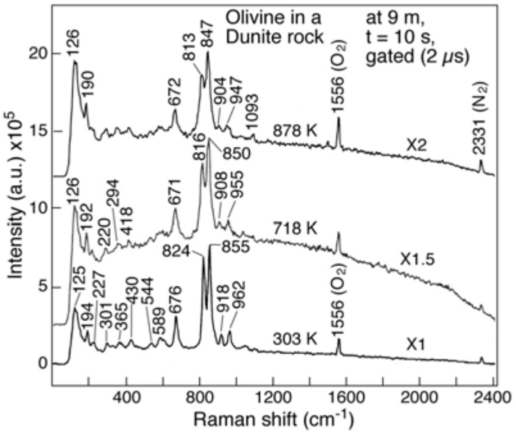

Figure 3. Raman spectra of olivine in dunite.

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 pressure and generating the plasma. The collisions between the expanding plasma and the supercritical CO_2 results 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. 2) 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. 3 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. 3 demonstrate that most of the Raman spectral features are observed with a properly gated spectrometer and a pulsed laser.

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 top image is the plasma (saturated intensity) under terrestrial conditions and the bottom image is the plasma under 93atm supercritical CO_2 at 423K. The image of the plasma is clearly distrorted 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 due to the orientation of the sample and is under investigation.

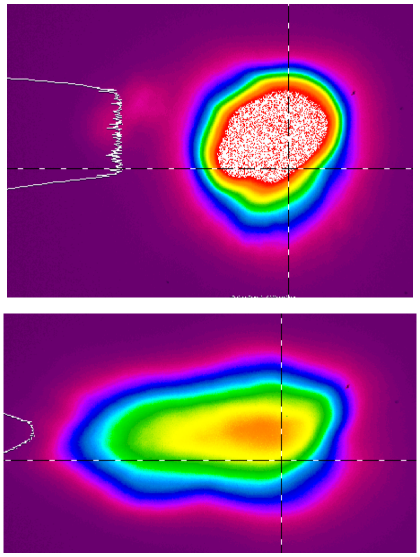

Figure 4. Image of the LIBS plasma generated in the supercritical CO_2 atmosphere.

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