

VENUS GEOCHEMICAL ANALYSIS BY REMOTE LASER-INDUCED BREAKDOWN SPECTROSCOPY (LIBS). S. M. Clegg¹, J. E. Barefield¹, R. C. Wiens¹, S. K. Sharma², A. K. Misra², J. Tucker³, M. D. Dyar³, J. Lambert⁴, S. Smrekar⁴, A. Treiman⁵. ¹Los Alamos National Laboratory, P.O. Box 1663 MS J565, Los Alamos, NM 87545, sclegg@lanl.gov, jbarefield@lanl.gov, rwiens@lanl.gov, ²Hawaii Institute of Geophysics and Planetology, University of Hawaii, 2525 Correa Rd., Honolulu, HI, 96822, sksharma@soest.hawaii.edu, anupam@hawaii.edu. ³Dept. of Astronomy, Mt. Holyoke College, South Hadley, MA 01075, mdyar@mtholyoke.edu. ⁴Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Dr., Pasadena CA, 91109; james.l.lambert@jpl.nasa.gov, ssmrekar@jpl.nasa.gov, ⁵Lunar and Planetary Institute, 3600 Bay Area Blvd., Houston TX 77058, treiman@lpi.usra.edu.

Introduction: The extreme Venus surface temperature (740K) and atmospheric pressure (92 bars) creates a challenging environment for future lander missions. 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 remotely determines both chemistry and mineralogy without the risks associated with collecting samples and bringing them into the lander. Raman and LIBS are highly complementary analytical techniques where Raman spectroscopy is used to determine the sample molecular structure and LIBS is employed to quantitatively determine the elemental composition. Wiens et al. [1] and Sharma et al. [2] demonstrated that these two complementary analytical techniques can be integrated into a single instrument suitable for planetary exploration.

This paper focuses on development of the LIBS technique to extract chemical composition and facilitate mineral/rock identification from LIBS spectra ac-

quired under Venus-like conditions. The total plasma intensity decreases somewhat as the pressure increases and interacts with the expanding plasma.[3] Despite these interactions, a robust LIBS plasma is produced because the estimated 1000 bar pressure within the plasma is still significantly greater than the Venus surface pressure. Furthermore, LIBS is insensitive to the 740 K Venus surface temperature because the 5000 K plasma temperature is so much greater than the 740K surface temperature.

Experimental: The LIBS experiments focus a Nd:YAG laser (1064nm, 10Hz, 50mJ/pulse) onto the surface of a 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 wavelengths diagnostic of the species present in the sample as they relax to lower electronic states. In these experiments, some of this emission was collected with a telescope and directed into a solarization resistant fiber connected to a dispersive spectrometer. The samples were placed 1.67m from the telescope in a cell filled with supercritical CO₂ at 92 bar and 423K, a temperature much lower than the 740K Venus surface temperature, resulting in a denser atmosphere.

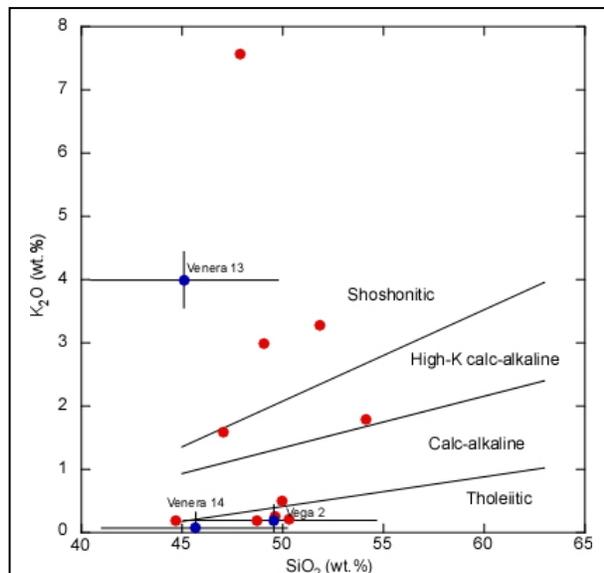
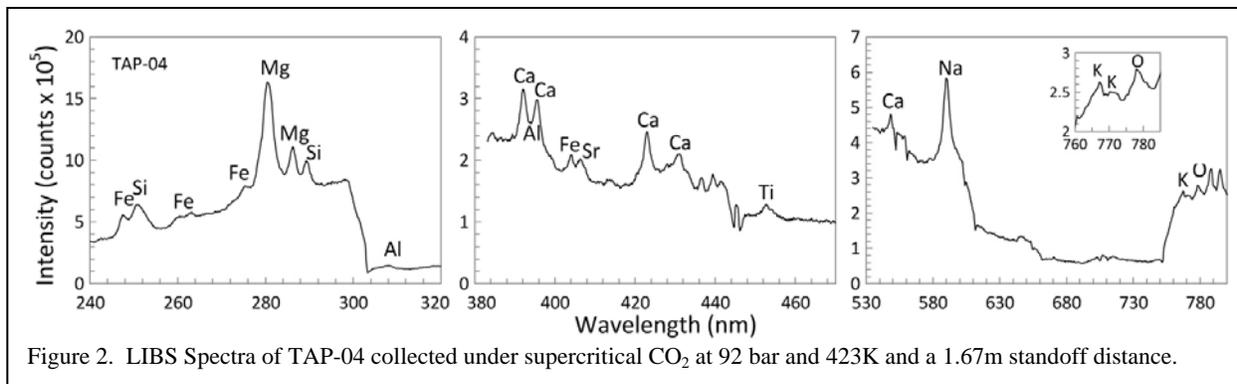


Figure 1. Comparison of Venus compositional data (blue [1]) with terrestrial standard samples used in this study (red). JA-1 is the most K-rich..

Table 1. Samples Studied

Sample	Rock Type	Source
TAP-04	Olivine minette	[5]
BHVO-2	Hawaiian basalt	USGS
BIR-1	Icelandic basalt	USGS
GBW-07105	Olivine basalt	NRCCRM, China
GUV BM	Basalt	Brammer
JB-2	Japanese basalt	Brammer
JA-1	Japanese andesite	GS Japan
Umphraville	Foidite	M. Rhodes
Cadillac	Basaltic trachy-andesite	M. Rhodes
Ultramafic	Dacite	M. Rhodes
KV04-17	Kauai volcanics	M. Rhodes
KV04-24	Kauai volcanics	M. Rhodes
KV04-25	Kauai volcanics	M. Rhodes



Sample Selection: Knowledge of the surface composition of Venus based on data from all landers suggests a surface composition that is primarily basaltic [4]. Samples for these experiments were chosen to be geochemically-likely on Venus, to approximate results from Soviet Venera and VEGA landers and reflect insights from other types of surface measurements on Venus (Table 1 and Figure 1).

Results and Discussion: Figure 2 shows a LIBS spectrum of the TAP-04 olivine minette sample. All of the major and some of the minor elements observed in this spectrum are identified. All of the emission lines are significantly broader than those observed under reduced pressure due to pressure broadening and spectrometer resolution. The optimum spectral resolution (ability to resolve neighboring peaks) will be influenced by pressure broadening, a consequence of collisions between the atoms and molecules in the plasma. In these experiments, the spectrometer resolution was reduced to improve the optical throughput and not limited by pressure broadening. Experiments are currently underway to identify the maximum spectral resolution that can be achieved.

Several multivariate analysis (MVA) techniques are employed to extract quantitative elemental abundance and determine sample identification[6]. Partial least squares analysis is a mathematical approach that correlates the elemental composition with the intensity variations from each pixel to generate a calibration model. Figure 3 contains a calibration model for Si. This model can be used to predict the elemental composition of an unknown samples. The PLS model accurately predicted the Si composition of the GUV BM sample (not included in the model calculations) as depicted in Figure 3. Principal Components Analysis (PCA) is another MVA approach used to identify the sample [6, 7]. PCA exploits only the spectral variations and can be used to classify the samples.

Conclusions: High quality LIBS spectra can be acquired under Venus surface conditions. Spectra were collected with several rock powder standards and

one rock sample and these spectra were used to generate a predictive PLS model.

Acknowledgments: We gratefully acknowledge the Los Alamos National Laboratory (LANL) Laboratory Directed Research and Development (LDRD) Exploratory Research (ER) Program for funding this work. We thank Kevin Righter for sample selection discussions and Kevin Righter, Michael Rhodes, Mac Rutherford, and Peter Hollings for providing samples.

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] Arp, Z.A. et al. (2004) *Spectrochim. Acta B* 59, 987-999 [4] Barsukov V. L. (1992) Venusian Igneous Rocks. In Venus Geology, Geochemistry, and Geophysics (eds. V. L. Barsukov, A. T. Basilevsky, V. P. Volkov, and V. W. Zharkov). Univ. Arizona Press, 65-176. [5] Righter K. and Rosas-Elguera J. (2001) *J. Petrol.*, 42, 2333-2361. [6] Clegg, S.M. et al. *Spectrochim. Acta B*, 64, 79-88. [7] Tucker, J. (2009) Calibrating ChemCam: Preparing to Probe the Red Planet. B.S. Thesis, Amherst College, <http://www.mtholyoke.edu/courses/mdyar/theses/JonTucker2009.pdf>

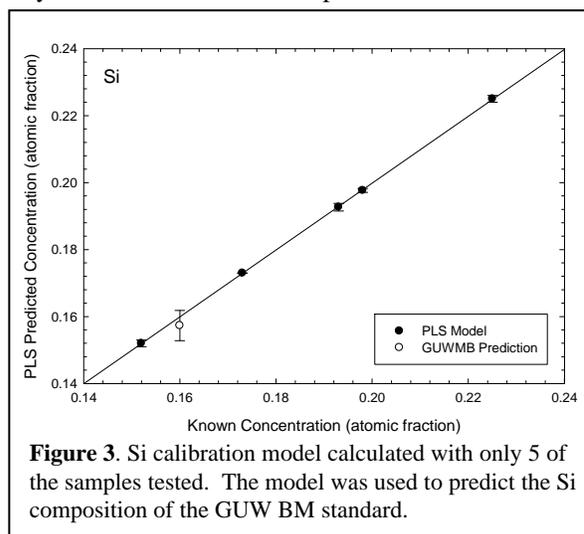


Figure 3. Si calibration model calculated with only 5 of the samples tested. The model was used to predict the Si composition of the GUV BM standard.