

RAMAN AND LASER-INDUCED BREAKDOWN SPECTROSCOPY (LIBS) GEOCHEMICAL ANALYSIS UNDER VENUS ATMOSPHERIC PRESSURE. S.M. Clegg¹, M.D. Dyar², S.K. Sharma³, A.K. Misra³, R.C. Wiens¹, S.E. Smrekar⁴, S. Maurice⁵ and L. Esposito⁶, ¹Los Alamos National Laboratory, P.O. Box 1663 MS J565, Los Alamos, NM 87545, sclegg@lanl.gov, ²Dept. of Astronomy, Mt. Holyoke College, South Hadley, MA 01075, ³Hawaii Institute of Geophysics and Planetology, University of Hawaii, 2525 Correa Rd., Honolulu, HI, 96822, ⁴Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Dr., Pasadena CA, 91109, ⁵Centre d'Etude Spatiale des Rayonnements (CESR), Toulouse, France, ⁶LASP - University of Colorado, 1234 Innovation Drive Boulder, Colorado 80303.

Session: On the Surface

Target: All Locations

Science Goal(s): II.A.1, II.B.1, II.B.2, III.A.3, III.B.2

Introduction: The extreme Venus surface temperature and atmospheric pressure create a challenging environment for landed missions. Venus geochemical investigations must be completed within several hours before the lander and instrument payload will be overcome by the harsh atmosphere. The Surface and Atmosphere Geochemical Explorer (SAGE) was one of the New Frontiers III candidate missions and it included a remote Raman – LIBS (RLS) instrument. RLS remotely determines both chemistry and mineralogy without the risks and time associated with collecting samples and bringing them into the lander. A RLS instrument can probe any surface target location from within the relative safety of the lander.

Raman and LIBS are highly complementary analytical techniques: Raman spectroscopy is used to determine the sample molecular structure and LIBS is employed to quantitatively determine the elemental composition. Clegg et al., [1] Wiens et al. [2] and Sharma et al. [3] demonstrated that these two complementary analytical techniques can be integrated into a single instrument suitable for planetary exploration. A RLS instrument similar to ChemCam [4,5] would record a Raman or LIBS spectrum from every laser shot resulting in >1,000 geochemical analyses within the first

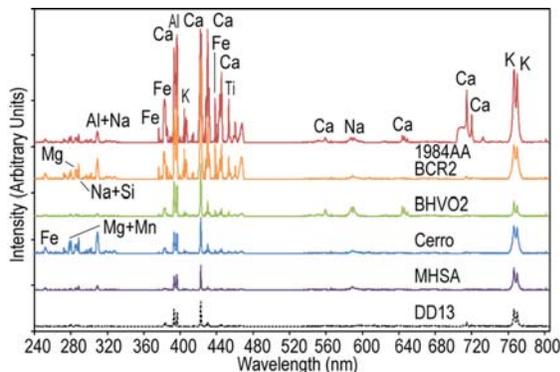


Figure 1. LIBS spectra collected with the JPL Venus chamber under 92 atm CO₂ at 740 K. All of the major elements are identified in the spectra.

two hours on the surface. Furthermore, the LIBS micron-scale depth profiles would be recorded from each location enabling the interrogation of weathered surfaces.

Experimental: LIBS experiments involve focusing a Nd:YAG laser (1064nm, 10Hz, 60mJ/pulse) onto a sample surface. The laser ablates material from the surface, generating an expanding plasma containing electronically excited atoms, ions and small molecules. These excited species emit light at wavelengths diagnostic of the species present in the sample. Some of this emission was collected with an 89 mm telescope and recorded with a dispersive (275 – 500nm) and customized miniature transmission spectrometer (535 – 800 nm) spectrometer as depicted in Figure 1.

Raman analyses such as those shown in Figure 2 involve directing the pulsed, doubled Nd:YAG laser (532 nm, 10Hz, 10 mJ/pulse) onto the sample surface.

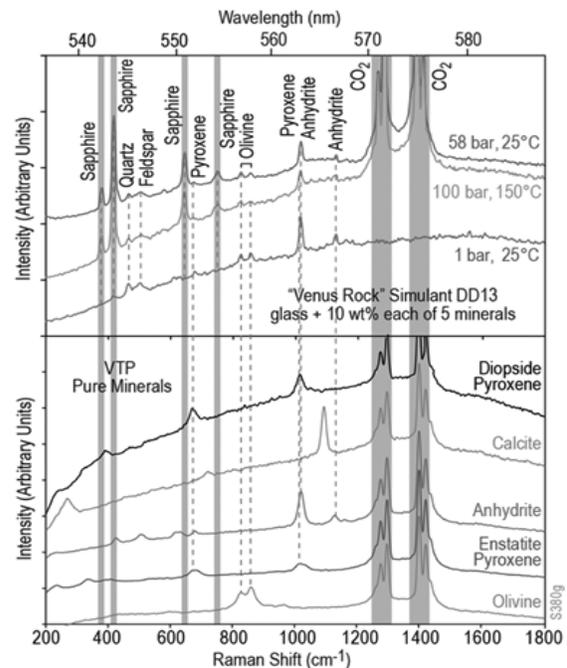


Figure 2. Raman spectra collected under 92 atm, 423 K (top) and 92 atm 740 K (bottom). The top spectra were collected from pressed powder of mixed minerals in a basaltic matrix while the bottom spectra are from natural mineralogical samples. The spectral regions highlighted in grey are from either the sapphire window or the CO₂.

The laser stimulates the Raman-active vibrational modes in the sample, producing Raman emission. Some of this emission is collected with the same 89 mm telescope and recorded with the same transmission spectrometer used in the LIBS experiments.

Results and Discussion: Figure 1 shows a LIBS spectrum of several a Venus-analog samples under 92 atm CO₂ and 740 K. All of the major elements and some of the minor elements are identified in the spectrum. LIBS plasma temperatures typically exceed 5000K and are completely insensitive to the Venus surface temperature. However, LIBS is sensitive to atmospheric pressure and the total LIBS emission intensity under Venus conditions is less than that observed under terrestrial or Martian conditions.[1,6]

The resulting LIBS spectra were processed using the same analytical methods developed for ChemCam. Each sample was analyzed in five separate locations with 100 laser shots each. The spectra were uploaded into the Unscrambler for Partial Least Squares analysis (PLS) [7-9]. Table 1 contains a list of preliminary LIBS elemental analysis requirements for a Venus surface mission

Figure 2 shows Raman spectra several pure minerals and synthetic mixtures. Raman spectra were collected under both ambient and under 1450 psi to model the influence of the Venus atmosphere on the Raman spectra. The dense CO₂ atmosphere produces two bright Raman lines that do not interfere with the mineralogical identification.

Raman spectroscopy is completely insensitive to the atmospheric pressure and are only slightly sensitive

to the sample temperature. Sharma et al. [8] demonstrated that the Raman peaks shifted by about 10 cm⁻¹ at 1273K, which is close to the spectrometer resolution. This small and predictable shift permits use of spectra acquired under ambient conditions for mineralogical identifications. Table 2 contains a list of preliminary Raman requirements for a Venus surface mission.

Conclusions: An integrated Raman and LIBS spectrometer is an ideal instrument for Venus geochemical and mineralogical investigations. RLS is rapid enough to acquire hundreds of mineralogical and elemental observations within the limitations of Venus surface operations. Integrated RLS mineralogical and elemental results will be presented.

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References: [1] Clegg S.M. et al., (2014) *Appl. Spectrosc.*, in press. [2]Wiens R. C., et al. (2005) *Spectrochim. Acta A* 61, 2324-2334. [3] Sharma, S. K. et al. (2007) *Spectrochim. Acta A*, 68, 1036-1045 (2007). [4] Maurice et al. (2012) *Space Science Reviews*, 170, 95-166. [5] Wiens et al. (2012) *Space Science Reviews*, 170, 167-227. [6]Arp, Z.A. et al. (2004) *Spectrochim. Acta B* 59, 987-999 [7] Clegg, S.M. et al. *Spectrochim. Acta B*, 64, 79-88. [8] Tucker J. M. et al. (2011) *Chem. Geol.*, 277, 137-148. [9] Wiens et al. (2013) *Spectrochim. Acta B* 82, 1-27.

Table 1: Some LIBS Requirements

Element	Units	Detection Limits Requirement	Accuracy Requirement (Absolute)	Bench-marked Errors ¹	Bench-marked 1-σ ²
SiO ₂	wt.%	2	±5-10%	±2.45	1.55
Al ₂ O ₃	wt.%	2	±5-10%	±1.64	1.51
Fe ₂ O ₃	wt.%	2	±5-10%	±1.50	1.18
CaO	wt.%	2	±5-10%	±0.82	1.06
MgO	wt.%	2	±5-10%	±1.88	1.57
Na ₂ O	wt.%	5	±10-20%	±0.62	0.49
K ₂ O	wt.%	5	±10-20%	±0.55	0.44
TiO ₂	wt.%	5	±10-20%	±0.38	0.38
MnO	wt.%	5	±10-20%	±0.03	0.02
P ₂ O ₅	wt.%	<0.01	±20%	±0.24	0.17
Cr ₂ O ₃	ppm	5	±10-20%	±170	n.d.
S	ppm	5	±5-10%	~1.0	n.d.

¹Errors based on 140 spectra of rocks and minerals acquired under ChemCam conditions, expressed as root mean square errors, from Dyar et al., (2010c). ²Values based on 10 repeated measurements of a single basaltic rock sample under Mars conditions, from Tucker et al. (2010).

Table 2: Raman Requirements

Mineral Group	Detection Limits Requirement	Accuracy Requirement (Absolute)	Bench-marked Detection Limits ¹	Bench-marked Accuracy ²
Primary anhydrous silicates	1-3	±10-15%	1	5
Secondary anhydrous silicates	1-3	±10-15%	1	5
Volatile-bearing silicates	1-3	±10-15%	1	5
Anhydrous sulfates	1-3	±10-15%	1	5
Anhydrous carbonates	1-3	±10-15%	1	5

Measurement capabilities benchmarked October 2010 and as reported in, e.g., Kontoyanis et al. (1997); Stopar et al. (2005).

¹Detection Limit is defined as the minimum modal % of each mineral that can be detected from among Raman-active materials

²Accuracy is defined as the vol% measured of each mineral as the standard deviation of ten repeated measurements.