

RAMAN & LASER-INDUCED BREAKDOWN SPECTROSCOPY (LIBS) REMOTE GEOCHEMICAL ANALYSIS UNDER VENUS ATMOSPHERIC PRESSURE. S.M. Clegg¹, S.K. Sharma², A.K. Misra², M.D. Dyar³, N. Dallmann¹, R.C. Wiens¹, D.T. Vaniman¹, E. A. Speicher³, S.E. Smrekar⁴, A. Wang⁵, S. Maurice⁶, and L. Esposito⁷. ¹Los Alamos National Laboratory, P.O. Box 1663 MS J565, Los Alamos, NM 87545, sclegg@lanl.gov, ²Hawaii Institute of Geophysics and Planetology, University of Hawaii, 2525 Correa Rd., Honolulu, HI, 96822, ³Dept. of Astronomy, Mt. Holyoke College, South Hadley, MA 01075, ⁴Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Dr., Pasadena CA, 91109, ⁵Earth & Planetary Sciences, Washington University, 1 Brookings Dr, Saint Louis MO 63130, ⁶Centre d'Etude Spatiale des Rayonnements (CESR), Toulouse, France, ⁷LASP - University of Colorado, 1234 Innovation Drive Boulder, Colorado 80303.

Introduction: The extreme Venus surface temperature (740K) and atmospheric pressure (92 bars) create a challenging environment for lander missions. Venus geochemical investigations must be completed within several hours of the landing before the lander and instrumentation will be overcome by the harsh atmosphere. The Surface and Atmosphere Geochemical Explorer (SAGE) was one of the New Frontiers III candidate missions; 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. 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. 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.

Sample Selection: Knowledge of the surface composition of Venus based on data from previous landers suggests a primarily basaltic surface composition [3]. These landers collected one geochemical sample, made one direct elemental measurement, and inferred the rock type and geochemistry. An RLS instrument would be capable of making more than a thousand geochemical and elemental observations of the same sample within a two hour surface mission and make direct

mineralogical observations for the first time.

This investigation focuses on analyses of 18 synthetic Venus-analog samples containing a complex mixture of minerals including anhydrite, forsterite, diopside, tremolite, chlorapatite, labradorite, apatite, α -quartz, olivine, and pyroxene to demonstrate the quantitative sensitivity of a combined Raman – LIBS instrument.

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. The excited species emit light at wavelengths diagnostic of the species present in the sample as they relax to lower electronic states. Some of this emission was collected with an 89 mm telescope and a dispersive (275 – 500nm) and customized miniature transmission spectrometer (535 – 800 nm) spectrometer.

The Raman experiments involve directing the pulsed, doubled Nd:YAG laser (532 nm, 10Hz, 10 mJ/pulse) onto the sample surface. The laser stimulates the Raman-active vibrational modes in the sample, producing the 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.

Samples probed with Raman and LIBS were placed 2.0 m from the telescope in a cell filled with supercritical CO₂ at 92 bar and 423K, a temperature much lower

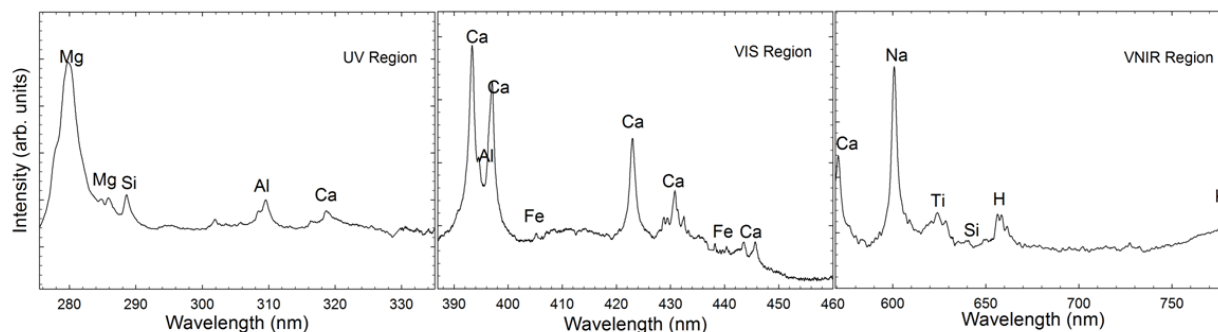


Figure 1. LIBS spectrum of the synthetic Venus-analog sample #13 containing 10 volume% amounts of anhydrite, olivine, labradorite, and quartz in a Fe-rich glass matrix collected under 92 atm and 423 K.

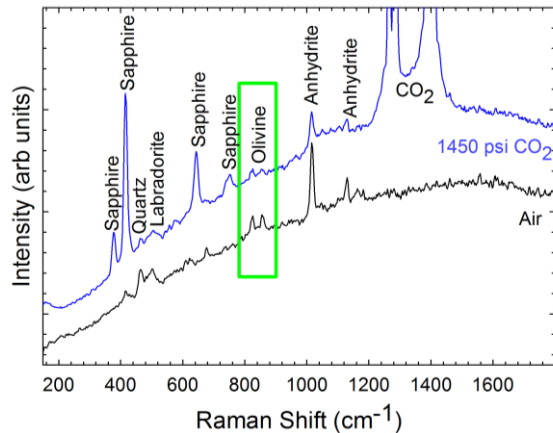


Figure 2. Raman spectra of the same synthetic sample probed by LIBS in Figure 1 containing anhydrite, olivine, labradorite feldspar, and α -quartz. These spectra demonstrate how molecular fingerprints are used to identify the mineralogical composition.

than the 740K Venus surface temperature, resulting in a more dense atmosphere.

Results and Discussion: Figure 1 shows a LIBS spectrum of a Venus-analog sample containing 10% anhydrite, 10% olivine, 10% labradorite, and 10% quartz in a 60% (by volume) Fe-rich glass matrix collected under 92 atm and 423 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.[4] These experiments are expected to be the worst case because the samples are in a denser atmosphere than Venus' due to the relatively low 423K temperature.

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. Spectra from each of these 100 shots were averaged to produce one spectrum per location and five spectra per sample. The background from each spectrum was removed and uploaded into the Unscrambler for Partial Least Squares analysis (PLS) [6,7].

Figure 2 shows Raman spectra of the same mineral/glass mixture probed with LIBS and depicted in Figure 1. The first 1500 cm^{-1} comprise the fingerprint region where unique mineralogical signatures are recorded. Raman spectra were collected under both ambient (black) and under 1450 psi (blue) to model the influence of the Venus atmosphere on the Raman spectra. The dense CO_2 atmosphere produces two bright Raman lines in the 1200 – 1400 cm^{-1} region. These are con-

veniently positioned towards the end of the fingerprint region and do not interfere with the mineralogical identification. The sapphirine windows also produce Raman emission lines that could have been avoided with higher quality sapphirine windows or using a shorter ICCD gate.

In contrast to LIBS, Raman spectroscopy is completely insensitive to the atmospheric pressure. Raman spectra were 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.

Olivine produced the weakest Raman emission in the set of minerals included in these experiments. However, the olivine emission lines are clearly observed in Figure 2 and were observed in other samples in our suite with only 1 volume% concentrations. Moreover, the olivine lines are sensitive to composition, making it possible to accurately determine composition within 10 mol% Fa/Fo.[9]

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.

Acknowledgments: We gratefully acknowledge the Los Alamos National Laboratory (LANL) Laboratory Directed Research and Development (LDRD) Exploratory Research (ER).

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 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. [4] Arp, Z.A. et al. (2004) *Spectrochim. Acta B* 59, 987-999 [5] Richter 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. M. et al. (2011) *Chem. Geol.*, 277, 137-148. [8] Sharma, S. K. et al. *Phil. Trans. Royal. Soc. A*, 368, 3167 – 3191. [9] Kuebler K. E. et al. (2006), *Geochim. Cosmochim. Acta*, V70, p6201-6222.