REMOTE RAMAN – LASER INDUCED BREAKDOWN SPECTROSCOPY (LIBS) GEOCHEMICAL INVESTIGATION UNDER VENUS ATMOSPHERIC CONDITIONS.
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Introduction: Extreme surface temperatures (~740 K) and atmospheric pressures (~92 bars) on Venus create a challenging environment for lander missions. Venus geochemical investigations must be completed within several hours of landing. The Surface and Atmosphere Geochemical Explorer (SAGE), one of the New Frontiers III candidate missions, includes a remote Raman–LIBS (RLS) instrument that can determine 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 because they can determine both molecular structure (mineralogy) and elemental composition, respectively. Wiens et al. [1] and Sharma et al. [2] demonstrated that they can be integrated into a single instrument suitable for planetary exploration. Here we present Raman and LIBS data acquired under Venus-analog conditions to show the feasibility of obtaining high-quality geochemical data from Venus.

Figure 1. Raman spectra measured at 99 bars and 423K samples containing 10 volume% amounts of anhydrite, olivine, labradorite (feldspar), and quartz in a Fe-rich glass matrix. The sapphire peaks are from the sapphire window on the pressure cell.

Table 1. Samples Studied by Raman and/or LIBS at VTP

Sample		Description
BHVO-2	a	Halemaumau basalt, USGS standard
GUW BM	a	Basalt, Brammers standard
GBW07105	a	(GSR-3) Basalt from NRCCRM, China
Ja-1	a	Andesite, Geological Society of Japan
TAP-4	a	Olivine minette [5]
DD13	a	anhydrite, labradorite, quartz, olivine
SARM-40	b	Carbonatite, Mintek
GBW-07103	b	Granite from NRCCM, China
KV04-17	b	Kauai volcanics, M. Rhodes
KV04-25	b	Kauai volcanics, M. Rhodes
LLC	b	Liw Liw creek, Phillipines shoshonite

15 mixtures of pure minerals and Fe-rich glass, simulating possible Venus mineralogy for SO_2-weathered basalts [4].

Sample Selection: Major element analyses from the Venera and Vega landers [3] suggest the presence of basaltic rock types along with variable amounts of S, either as a primary constituent or as a secondary product of atmospheric interactions. Using these chemical results as starting points, Venus mineralogy models predict that the surface is composed of pri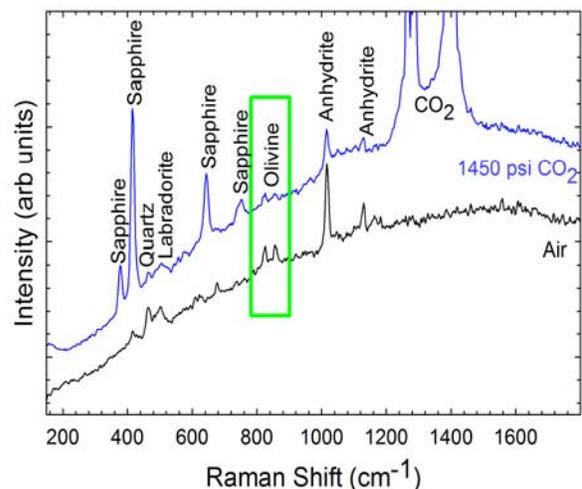mary basaltic minerals, glass (as unreacted residua) and specific alteration minerals. Accordingly, sample sets with extrusive igneous rocks and Venus-analog primary and secondary (alteration phase) minerals were used in this study (Table 1). Some were probed by both Raman and LIBS to demonstrate the benefits of the paired analyses. Rock powder standards were analyzed to calibrate the LIBS technique and demonstrate its quantitative sensitivity. Results of a Raman study of complex mixtures of minerals including anhydrite, feldspar, apatite, quartz, olivine, and pyroxene are reported elsewhere [3], to demonstrate the Raman quantitative sensitivity.

Experimental: The Raman experiments direct a pulsed, doubled Nd:YAG laser (532 nm, 20Hz, 6 - 17 mJ/pulse) onto the sample surface 2 m away. The laser stimulates Raman active vibrational modes in the sample, producing the Raman emission. Some of this emission is collected with a 89 mm Questar Telescope and directed into a customized, miniature transmission spectrometer.

LIBS experiments focus a Nd:YAG laser (1064nm, 10Hz, 60mJ/pulse) onto the sample surface. The laser
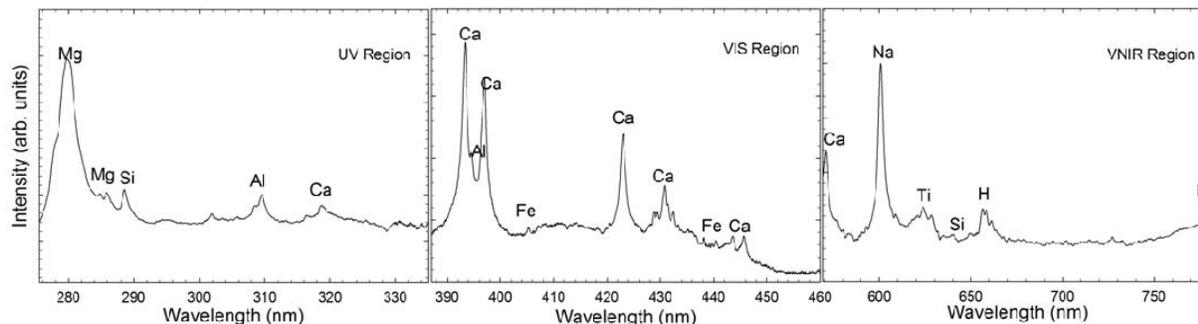
Figure 2. LIBS spectrum of the sample from Figure 1 containing 10 vol% amounts of anhydrite, olivine, labradorite, and quartz in a Fe-rich glass matrix collected under 92 bars and 423 K.

ablates material from the surface and generates an expanding plasma containing electronically excited atoms, ions, and small molecules. These emit light at wavelengths diagnostic of the species present as they relax to lower electronic states. Emission was collected with a telescope and directed into a dispersive (275–500 nm) and transmission (535–777 nm) spectrometer. Samples probed with Raman and LIBS were placed 2.0 m from the telescope in a Venus cell filled with supercritical CO_2 at 92 bars and 423 K, a temperature much lower than the 740 K Venus surface temperature.

LIBS data were processed using The Unscrambler, a commercially-available software product, for multivariate analysis using Partial Least Squares (PLS) regression. PLS is well suited to situations where there are many predictor variables (**X**; spectra) and few response variables (**Y**; elemental abundances).

Results and Discussion: Fig. 1 shows Raman spectra of a complex mixture of minerals at STP in air and under 99 bars CO_2 at 423 K. The first 1500 cm^{-1} is
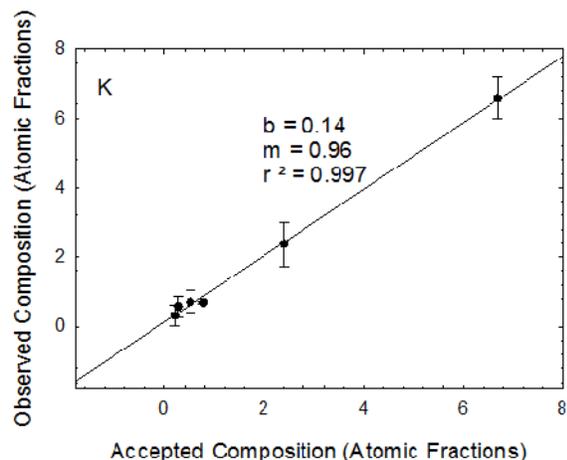

Figure 3. The LIBS calibration model results for K. The 0.997 R^2 is an indication of the accuracy while the error bars represent the precision of the measurement. The precision is influenced by both the analytical technique as well as the sample heterogeneity.

the fingerprint region where unique mineralogical signatures are recorded. The sample probed in Fig. 1 contains spectral signatures from the four minerals (e.g., olivine, labradorite, quartz, and anhydrite) present at 10 vol% under Venus conditions. Moreover, these signatures are also observed in spectra of Fe-rich glass with as little as 1 vol% of these mineral [4].

Fig. 2 presents the LIBS spectrum of the same mixed mineral sample depicted in the Fig. 1 Raman spectrum. All of the major elements and some of the minor elements are identified in the spectrum.

Spectra of six samples (labeled "a" in Table 1) were used to generate a calibration model of the LIBS technique for data acquired under Venus conditions. A validation plot for K generated from a PLS calibration model is shown in Fig. 3. Although the number of samples is small, this and the other validation plots for all the major elements analyzed (Si, Al, Ti, Fe, Mg, Mn, Ca, Na, and K) demonstrate the promise of acquiring quantitative chemical analyses from LIBS spectra. Follow-up work using both "a" and "b" group samples from Table 1 will further refine these models. Precision and accuracy of combined LIBS and Raman analyses will be sufficient to distinguish the origins of Venusian rocks using mineral assemblages in combination with standard geochemical classification schemes.

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] Sharma S.K. et al. (2011) this conference. [5] Righter K. and Rosas-Elguera J. (2001) *J. Petrol., 42*, 2333-2361.