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Remote Raman – Laser Induced Breakdown Spectroscopy (LIBS) Geochemical Investigation under Venus Atmospheric Conditions

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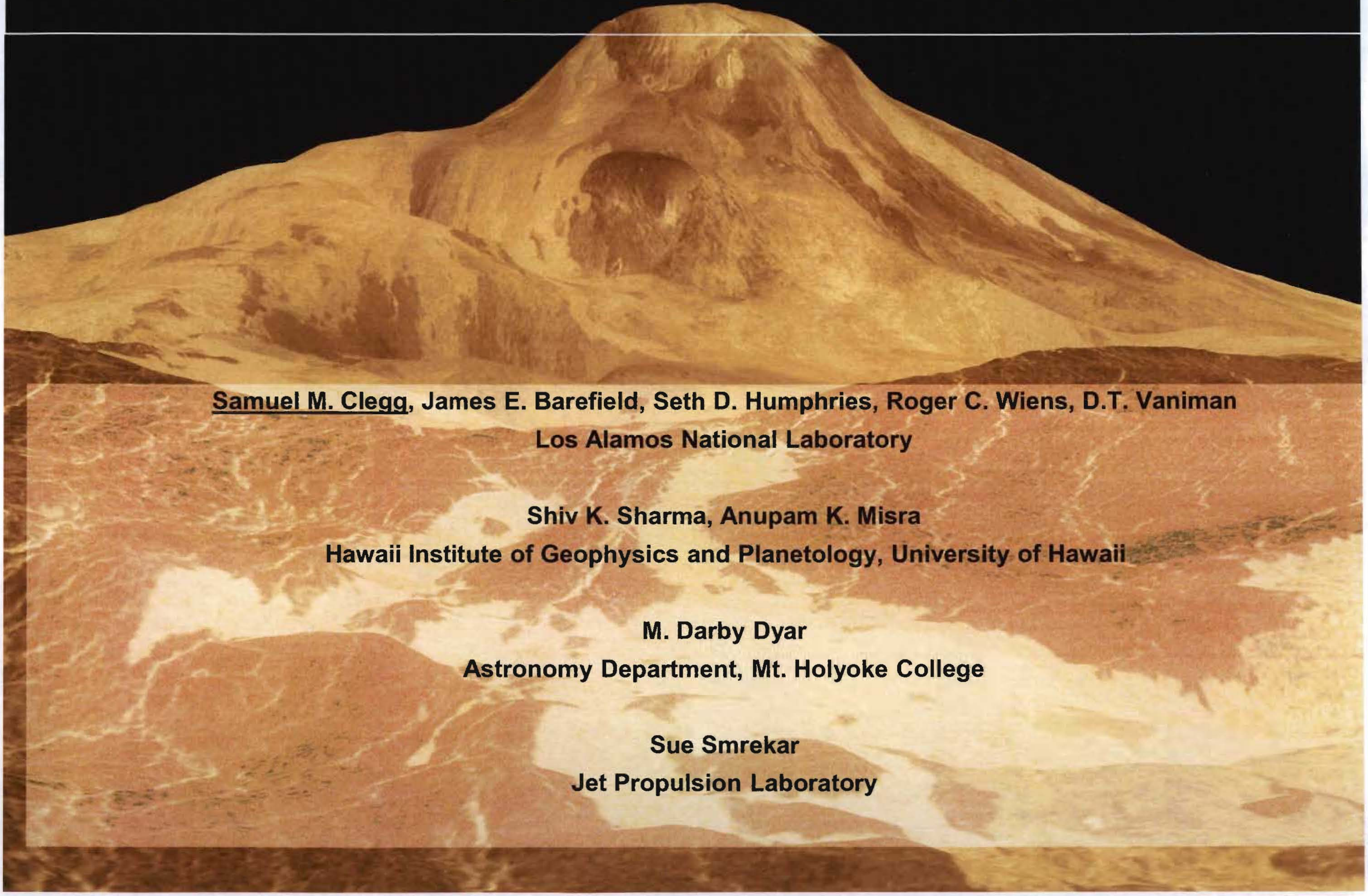
The extreme Venus surface temperatures (~740 K) and atmospheric pressures (~93 atm) create a challenging environment for surface missions. Scientific investigations capable of Venus geochemical observations must be completed within hours of landing before the lander will be overcome by the harsh atmosphere. 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] demonstrated that both analytical techniques can be integrated into a single instrument capable of planetary missions. The focus of this paper is to explore the capability to probe geologic samples with Raman – LIBS and demonstrate quantitative analysis under Venus surface conditions.

Raman and LIBS are highly complementary analytical techniques capable of detecting both the mineralogical and geochemical composition of Venus surface materials. These techniques have the potential to profoundly increase our knowledge of the Venus surface composition, which is currently limited to geochemical data from Soviet Venera and VEGA landers that collectively suggest a surface composition that is primarily tholeiitic basaltic [3] with some potentially more evolved compositions and, in some locations, K-rich trachyandesite. These landers were not equipped to probe the surface mineralogy as can be accomplished with Raman spectroscopy. Based on the observed compositional differences and recognizing the imprecise nature of the existing data, 15 samples were chosen to constitute a Venus-analog suite for this study, including five basalts, two each of andesites, dacites, and sulfates, and single samples of a foidite, trachy-andesite, rhyolite, and basaltic trachyandesite under Venus conditions. LIBS data reduction involved generating a partial least squares (PLS) model with a subset of the rock powder standards to quantitatively determine the major elemental abundance of the remaining samples [4]. PLS analysis suggests that the major element compositions can be determined with root mean square errors ca. 5% (absolute) for SiO_2, Al_2O_3, Fe_2O_3(total), MgO, and CaO, and ca. 2% or less for TiO_2, Cr_2O_3, MnO, K_2O, and Na_2O. Finally, the Raman experiments have been conducted under supercritical CO_2 involving single-mineral and mixed-mineral samples containing talc, olivine, pyroxenes, feldspars, anhydrite, barite, and siderite. The Raman data have shown that the individual minerals can easily be identified individually or in mixtures.

[1] Wiens R.C., et al. (2005) *Spect. Acta A* **61**, 2324; [2] Sharma, S. K. *et al.* (2007) *Spect. Acta A,* **68** , 1036 (2007); [3] Barsukov VL (1992) Venusian Igneous Rocks. In Venus Geology, Geochemistry, and Geophysics (eds. VL Barsukov *et al.*). Univ. Arizona Press, pp. 165-176. [4] Tucker, J.M. *et al.* (2010) *Chem. Geol.*, in press.

Remote Raman – Laser Induced Breakdown Spectroscopy (LIBS) Geochemical Investigation under Venus Atmospheric Conditions



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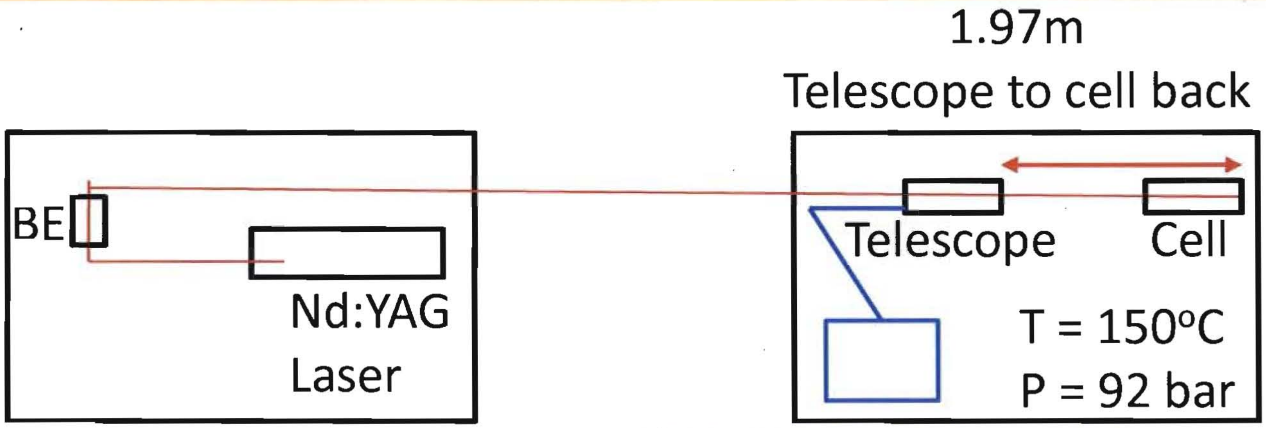
Venus Geochemical Challenges

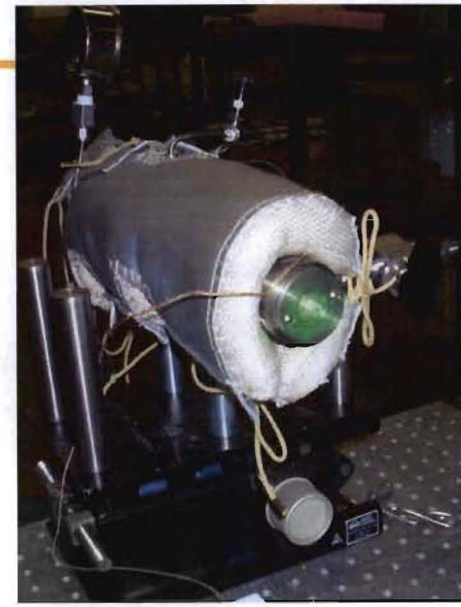
- **Surface and Geochemical Atmosphere Explorer (SAGE)**
  - Remote Raman and Laser – Induced Breakdown Spectroscopy (RLS)
  - No Sample Collection, No Interlocks
  - Probe Multiple Locations
  - Rapid Analysis
    - Typically Minutes / Spot
- **Venus Surface**
  - 92 bar, mostly CO_2
  - ~740 K
  - Landers Survive for Only Hours

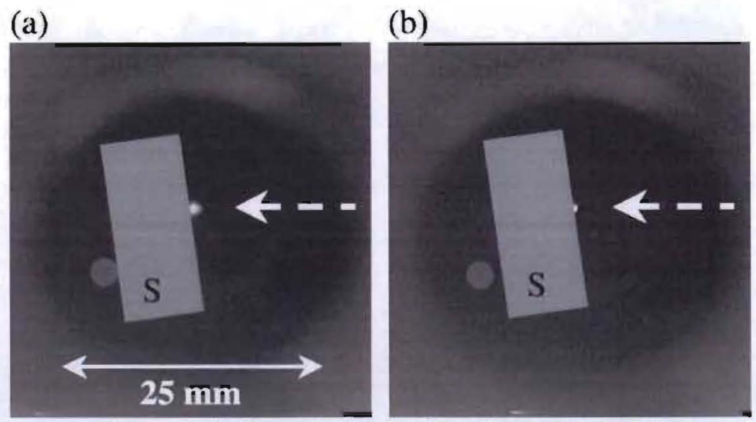
The LIBS Technique



1 laser, single pulse
~80mJ/pulse

Dispersive (240-480nm) and
Transmission (535-800nm)
Spectrometer with ICCD

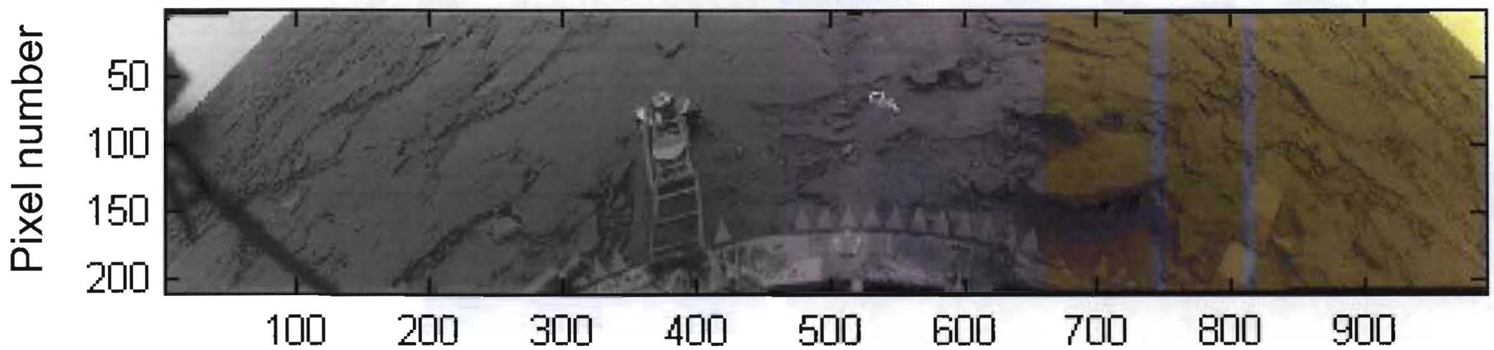




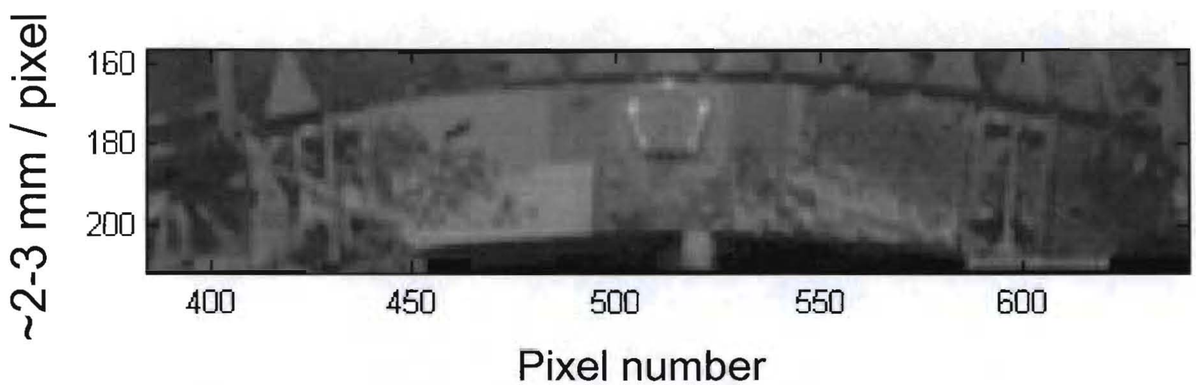
Arp et al. Spectrochim B. 59, 987, 2004.

Turbulence

Venera 14 Surface Images (~256 x 1024 pixels)



Lander ring "teeth" ~ 7 cm long, 4.3 cm wide at base
Pentagon on lander ring ~ 5 cm high, 5.3 cm wide



Turbulence

Refractive Index Structure Constant vs. Temperature Structure Constant

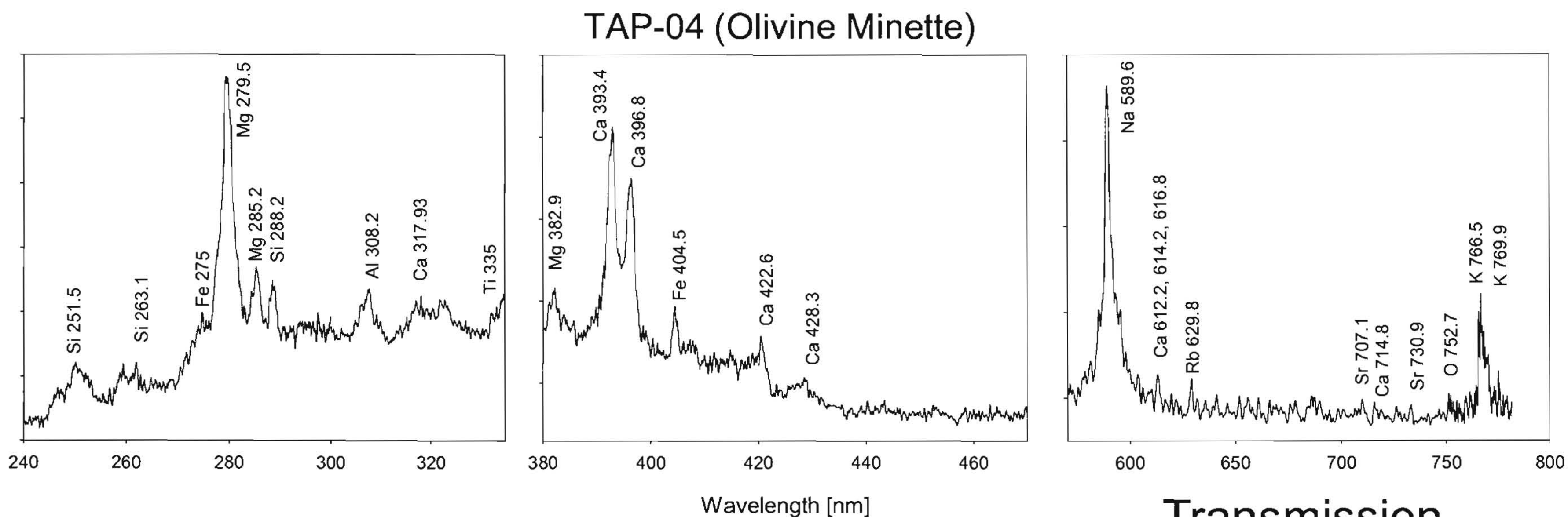
$$C_n^2 \sim \left(\alpha \frac{P}{T^2} \right)^2 \cdot C_T^2$$

Normally, P = 1 atm CO_2, T = 300K $C_n^2 \sim 1.23 \, x \, 10^{-10} \, \alpha^2 \cdot C_T^2$

On Venus, P ~ 90 atm CO_2, T ~ 750K $C_n^2 \sim 2.56 \, x \, 10^{-8} \, \alpha^2 \cdot C_T^2$

$$\frac{C^2_{n\,Venus}}{C^2_{n\,Earth}} \sim 720 \frac{C^2_{T_V}}{C^2_{T_E}}$$

LIBS Spectra



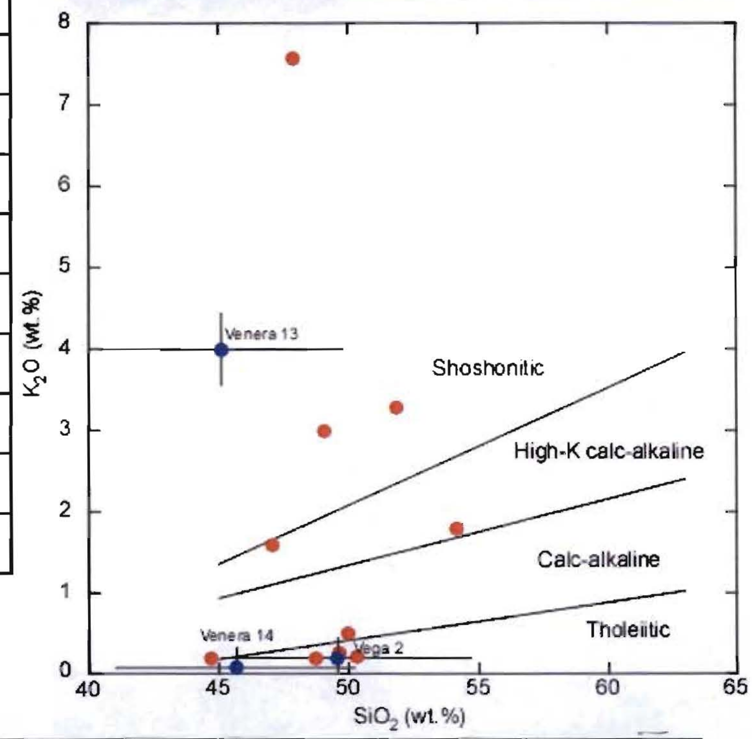
Dispersive Spectrometer

Transmission Spectrometer

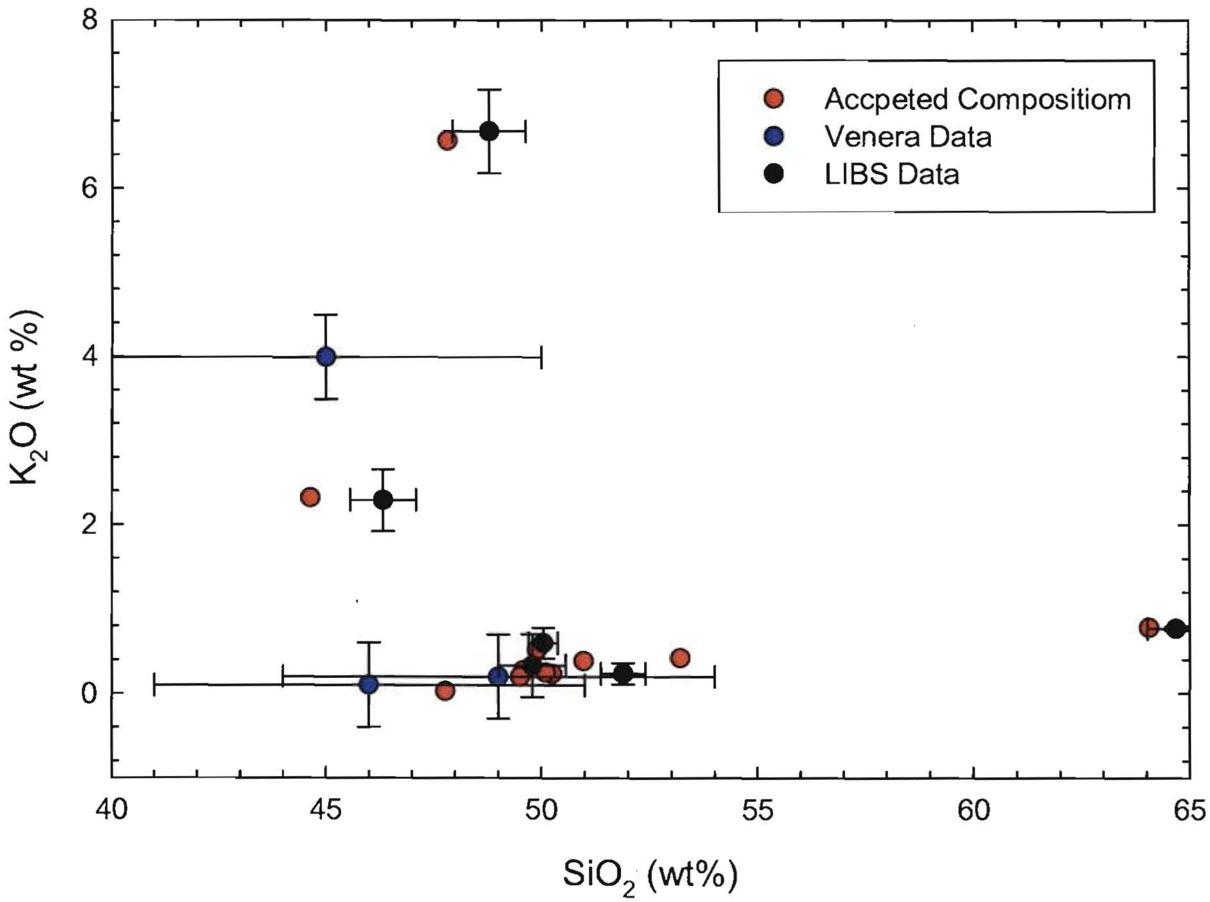
T = 150°C, P = 92 bar CO_2, 1.97 m standoff distance

Samples

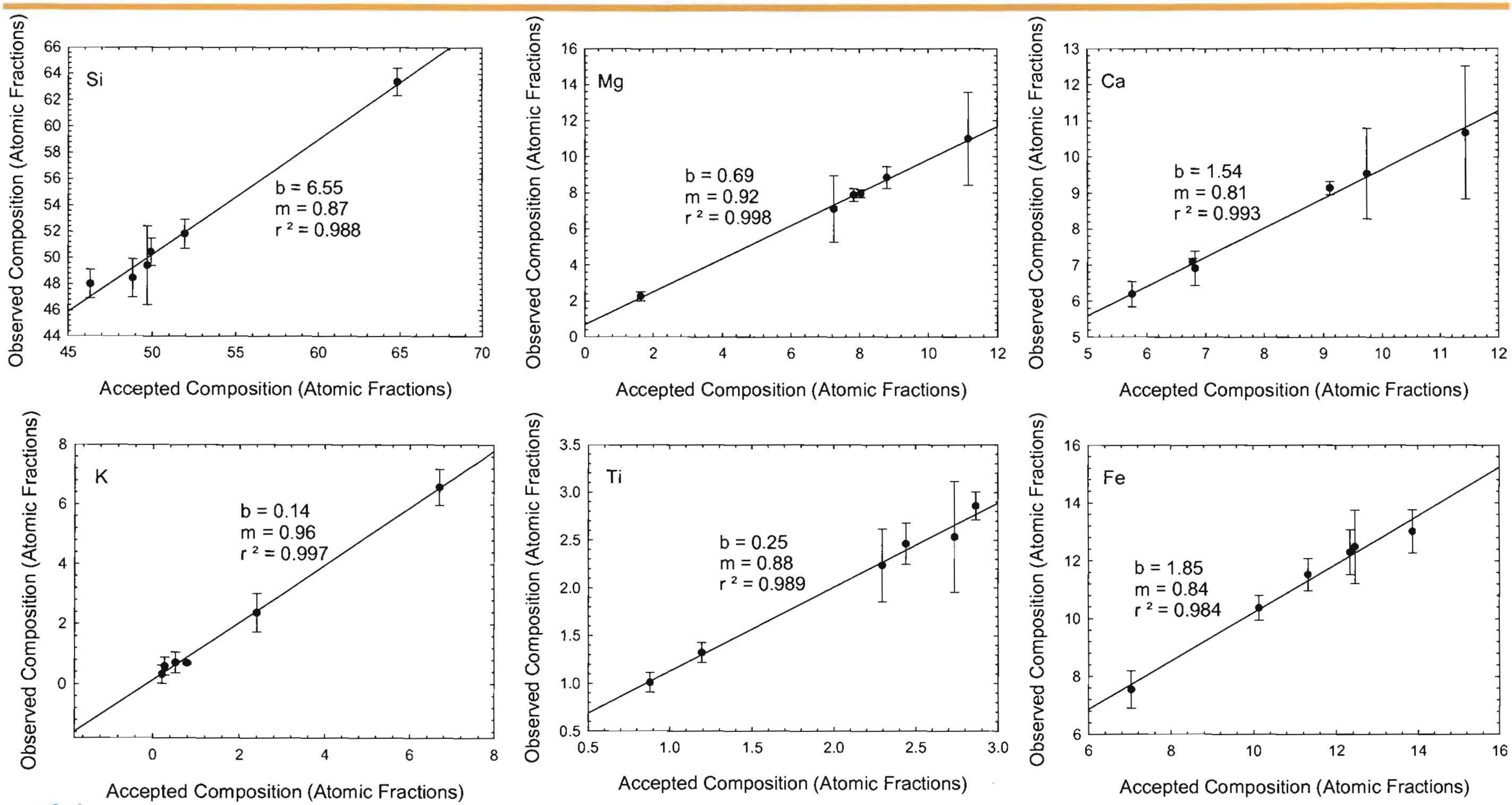
Sample	Rock Type	Source
TAP-04	Olivine minette	[5]
BHVO-2	Hawaiian basalt	USGS
BIR-1	Icelandic basalt	USGS
GBW-07105	Olivine basalt	NRCCRM, China
GUW BM	Basalt	Brammer
JB-2	Japanese basalt	Brammer
JA-1	Japanese andesite	GS Japan
Umphraville	Foidite	M. Rhodes
Cadillac	Basaltic trachy-andesite	M. Rhodes
Ultramafic	Dacite	M. Rhodes
KV04-17	Kauai volcanics	M. Rhodes
KV04-24	Kauai volcanics	M. Rhodes
KVO4-25	Kauai volcanics	M. Rhodes



Results – Partial Least Squares 2 Analysis



Results – Partial Least Squares 2 Analysis



Results – Partial Least Squares 2 Analysis

Sample	SiO2				Al2O3				MgO			
	Observed	%unc	Accepted	%D	Observed	%unc	Accepted	%D	Observed	%unc	Accepted	%D
GBW07105	48.01	2.28%	46.33	3.64%	13.73	4.90%	14.30	3.99%	7.95	2.66%	8.03	1.03%
JA-1	63.39	1.65%	64.84	2.24%	15.11	0.58%	15.16	0.36%	2.26	11.17%	1.62	38.90%
KV0425	49.41	6.09%	49.70	0.60%	12.79	9.94%	12.43	2.89%	10.99	23.36%	11.16	1.54%
TAP04	48.47	3.00%	48.83	0.76%	10.73	2.60%	10.58	1.45%	8.85	6.90%	8.78	0.69%
GUWBM	51.82	2.15%	51.94	0.25%	16.59	0.96%	17.03	2.58%	7.88	4.49%	7.82	0.72%
BHVO-2	50.44	2.11%	49.93	1.02%	13.76	15.53%	13.54	1.65%	7.11	25.80%	7.25	1.98%

Sample	CaO				Na2O				K2O			
	Observed	%unc	Accepted	%D	Observed	%unc	Accepted	%D	Observed	%unc	Accepted	%D
GBW07105	9.13	2.02%	9.11	0.21%	3.29	6.79%	3.496404	5.66%	2.37	26.99%	2.40	1.01%
JA-1	6.19	5.69%	5.75	7.71%	3.78	4.89%	3.907566	3.15%	0.693	5.10%	0.789	12.11%
KV0425	9.53	13.18%	9.74	2.20%	2.16	43.89%	1.918482	12.99%	0.580	51.19%	0.275	110.91%
TAP04	6.90	6.92%	6.82	1.22%	4.07	5.07%	4.079421	0.12%	6.57	9.20%	6.69	1.79%
GUWBM	7.09	1.24%	6.78	4.56%	4.60	0.11%	4.872788	5.55%	0.314	94.03%	0.209	49.96%
BHVO-2	10.66	17.20%	11.43	6.74%	2.47	59.70%	2.2272	11.09%	0.710	49.09%	0.521	36.14%

Sample	TiO2				Fe2O3T			
	Observed	%unc	Accepted	%D	average	%unc	accepted	%D
GBW07105	2.46	8.78%	2.44	0.86%	13.01	5.68%	13.86	6.12%
JA-1	1.01	10.14%	0.880	14.84%	7.54	8.53%	7.03	7.31%
KV0425	2.23	17.00%	2.29	2.60%	12.48	10.14%	12.45	0.19%
TAP04	2.85	5.12%	2.86	0.21%	11.52	4.90%	11.31	1.79%
GUWBM	1.32	7.86%	1.19	10.63%	10.37	4.21%	10.13	2.37%
BHVO-2	2.53	22.94%	2.73	7.51%	12.29	6.32%	12.34	0.40%

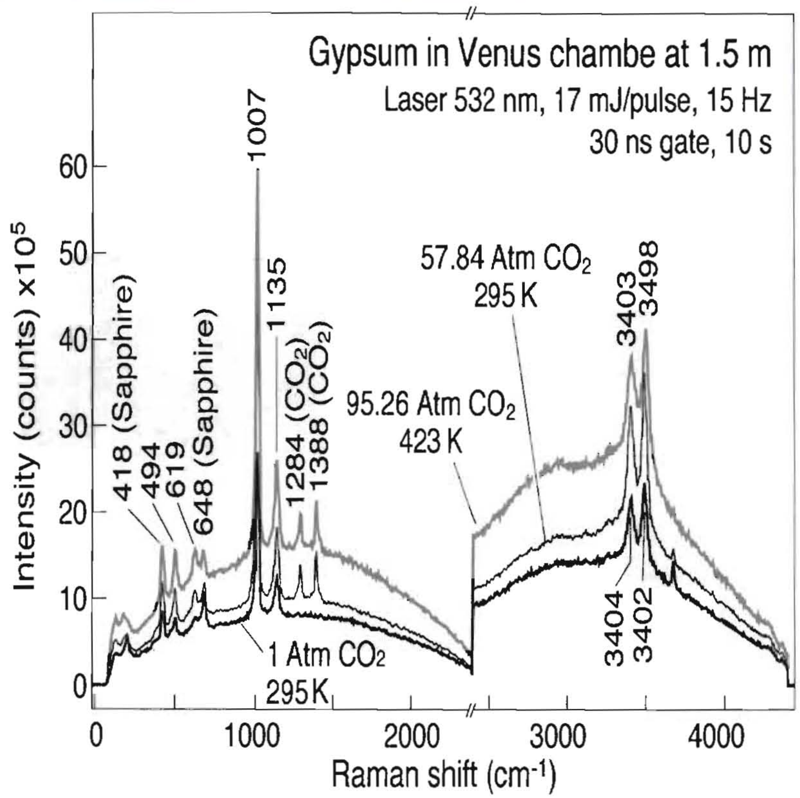
Raman Spectroscopy

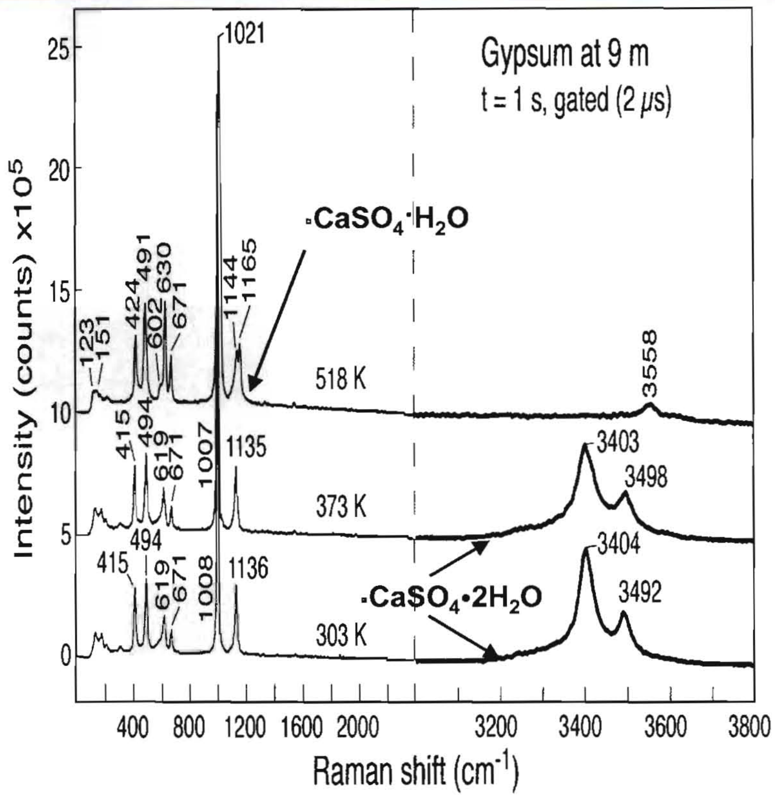
➢**Two of the most important advantages of time-resolved (TR) Raman spectroscopy** has over other techniques for a mission to Venus is <u>rapid mineralogical</u> analysis of both hydrous and anhydrous minerals and <u>stand-off analysis</u> at distances of many meters from a lander both during daytime and nighttimes. Rapid mineralogical analysis and stand-off analysis are very important to missions to Venus due to the harsh environment at the planet surface (90 atm, 735 K supercritical CO_2) and expected short lifetime (less than few hours) of the *in situ* surface lander with enhanced design.

➢Reports that under certain conditions a 248 nm laser beam failed to emerge from an optical cell containing supercritical CO_2 raised questions if the TR remote Raman spectra of the surface minerals can be obtained under Venus conditions or on Venus from a lander.

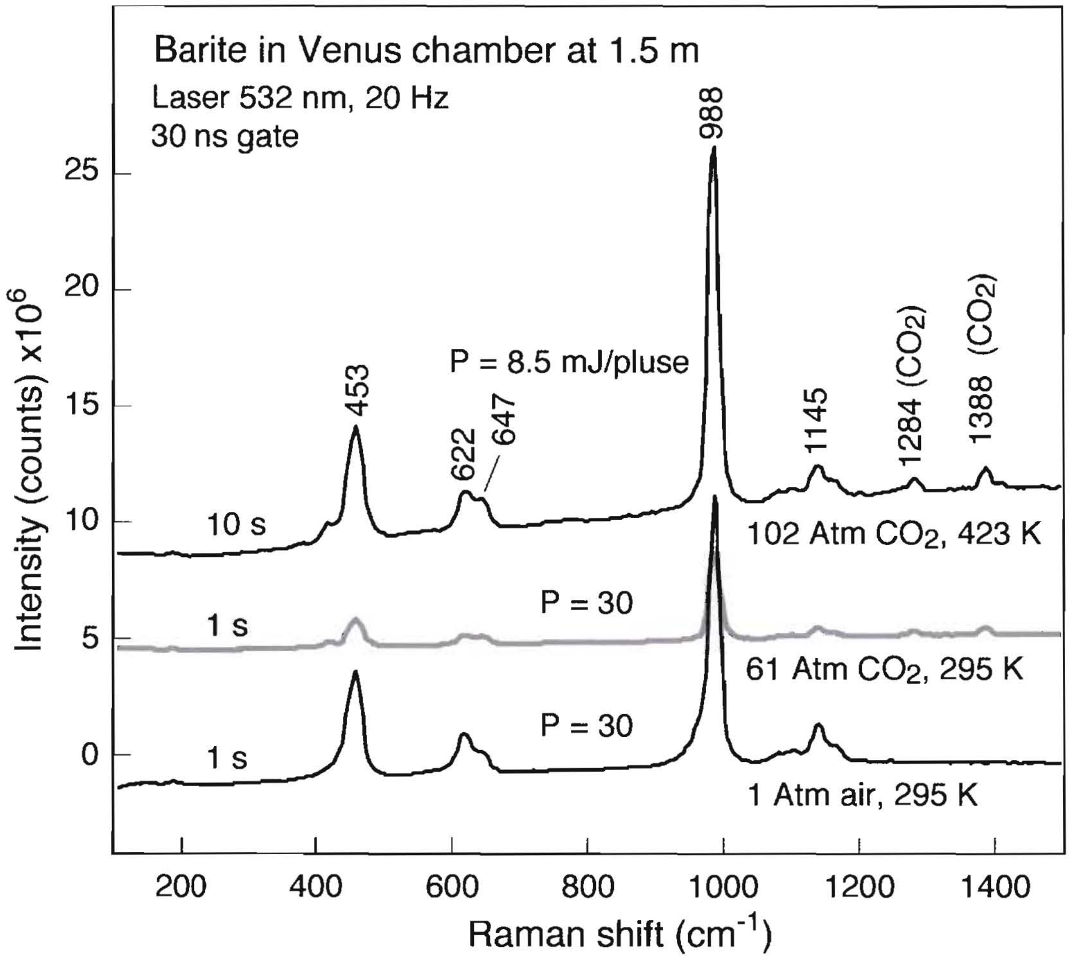
*No problem with 532 nm laser excitation was encountered in the current work.

Raman Spectra of Gypsum ($CaSO_4 \cdot 2H_2O$)

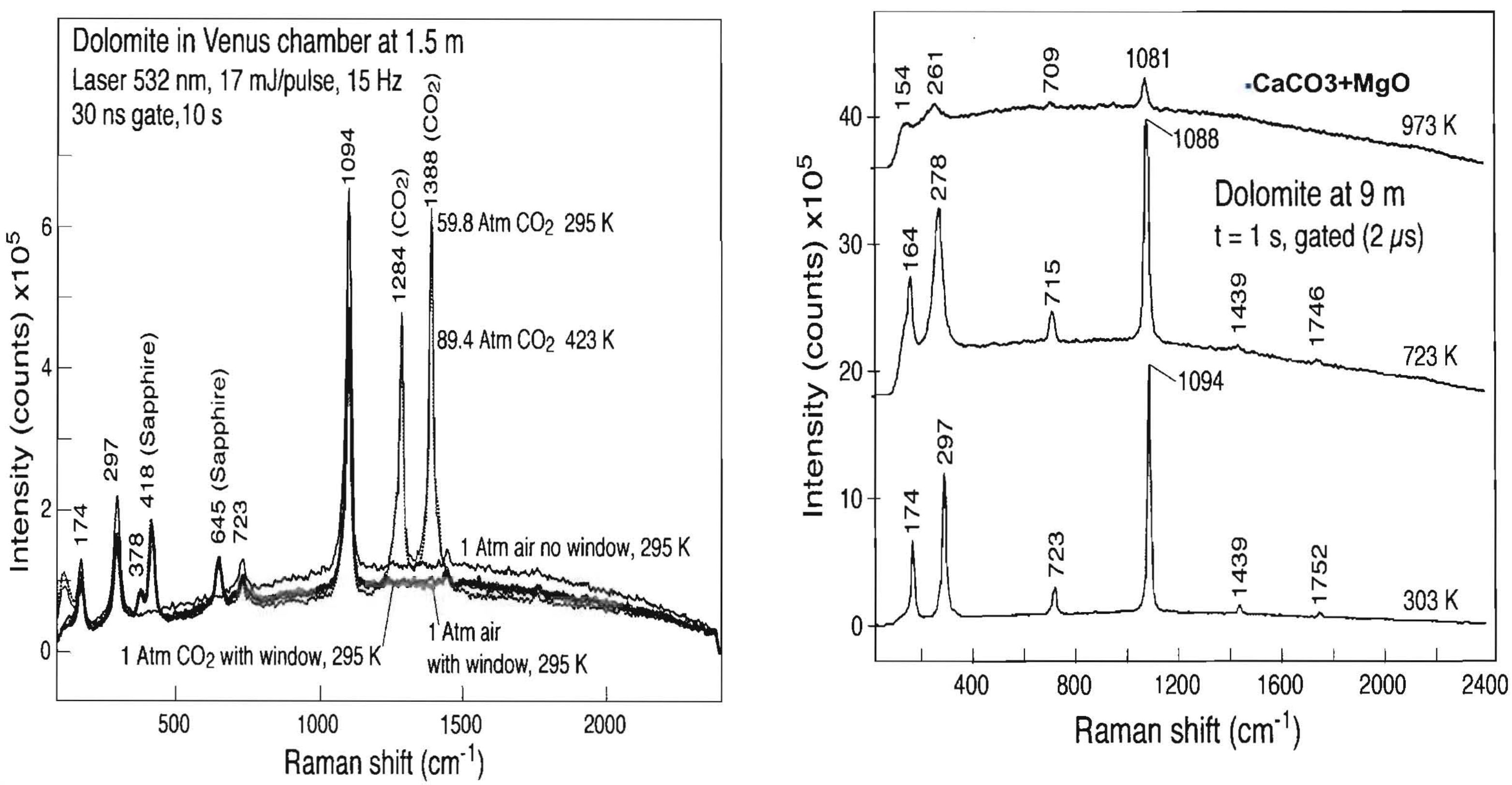




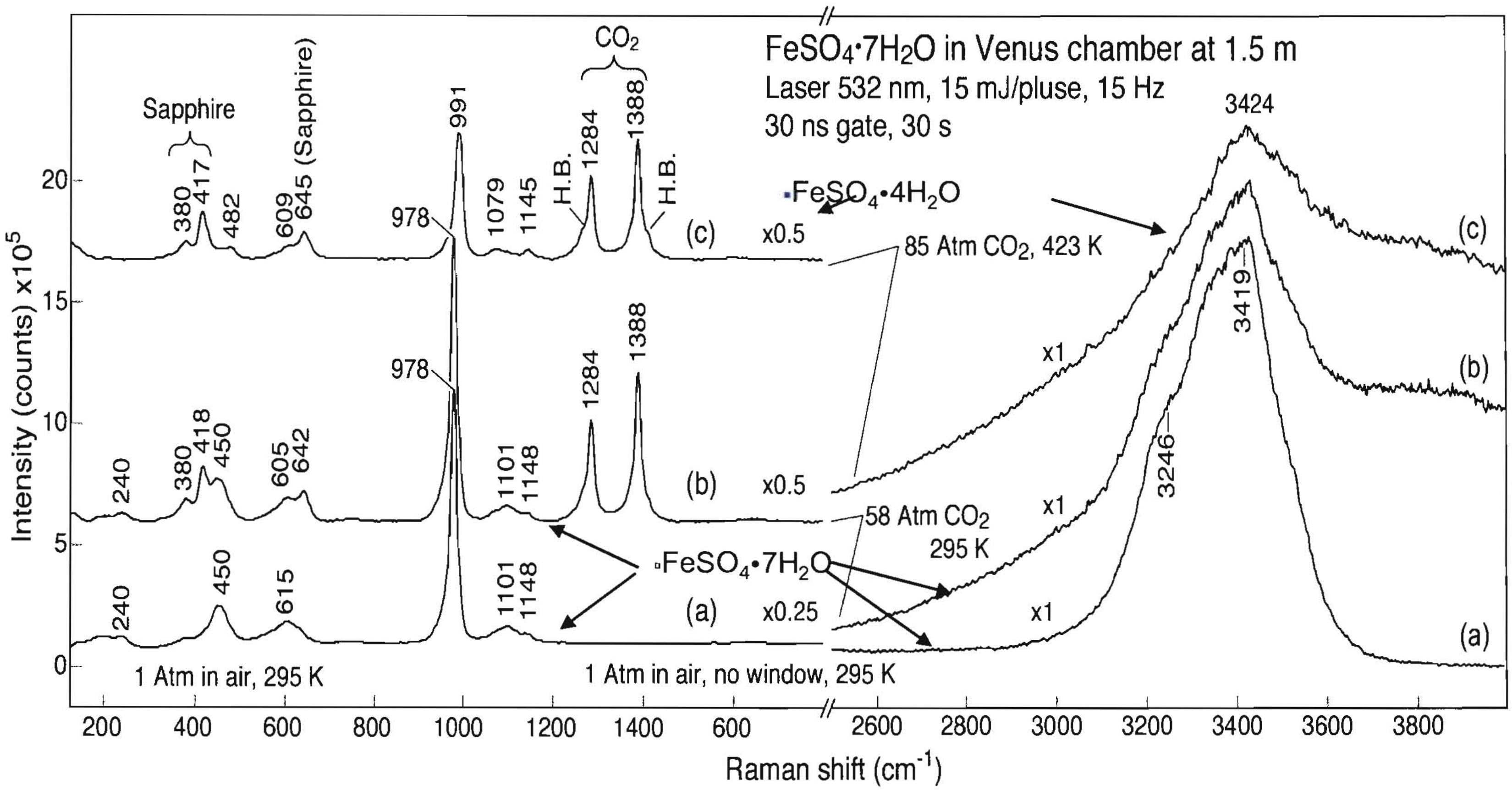
Raman Spectra of Barite



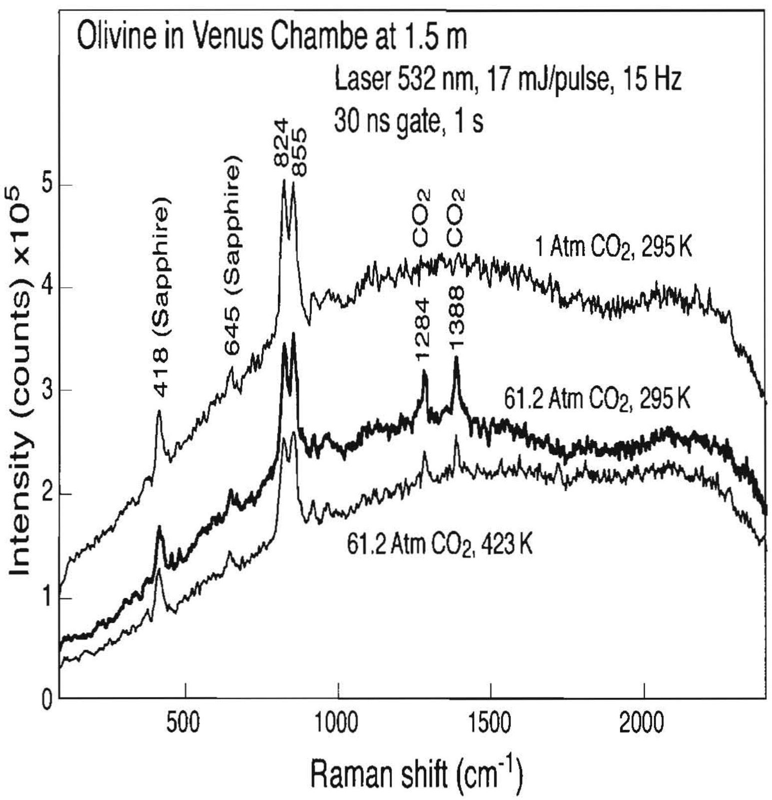
Raman Spectra of Dolomite

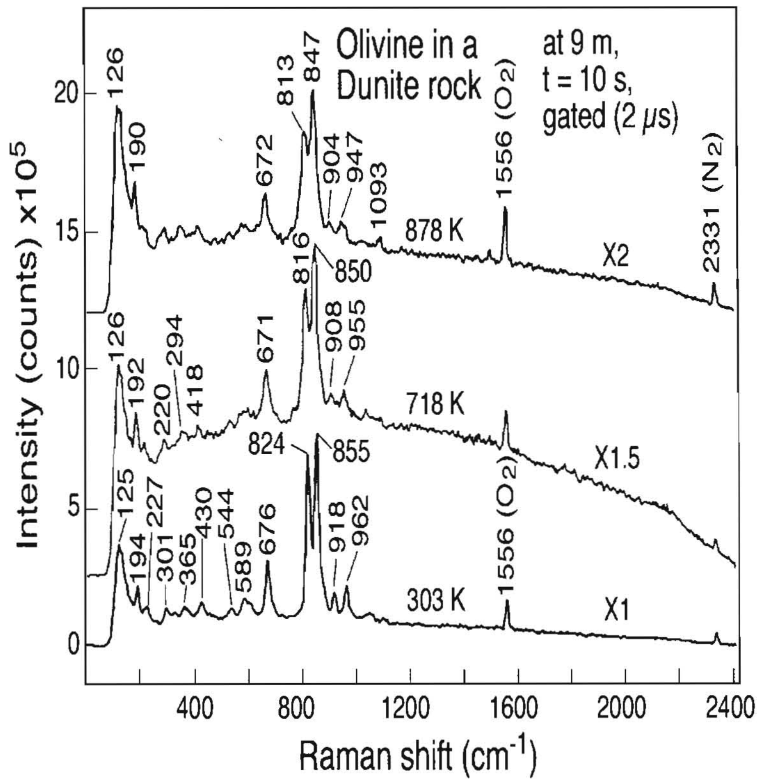


Raman Spectra of Iron Sulfate Hydrate

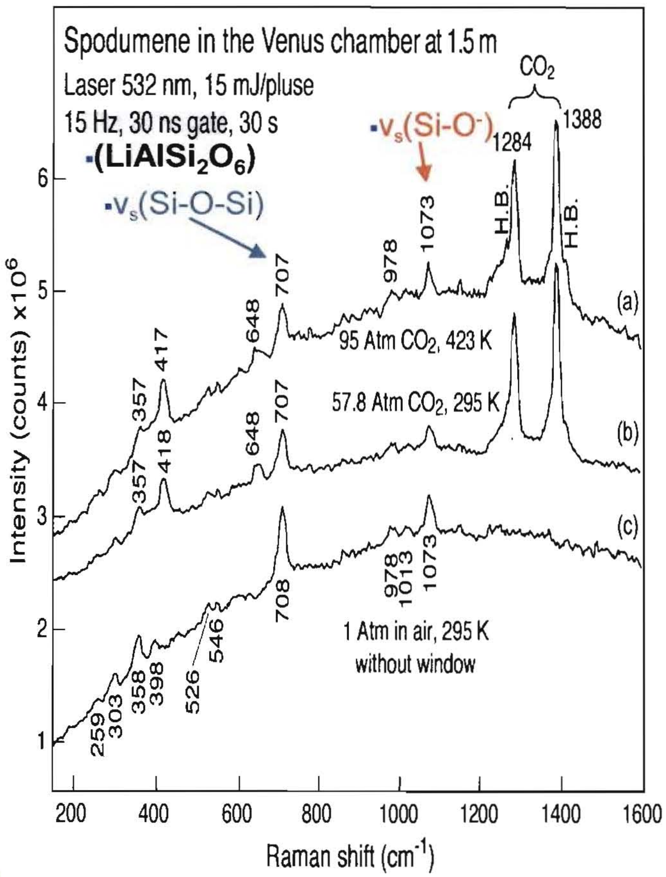


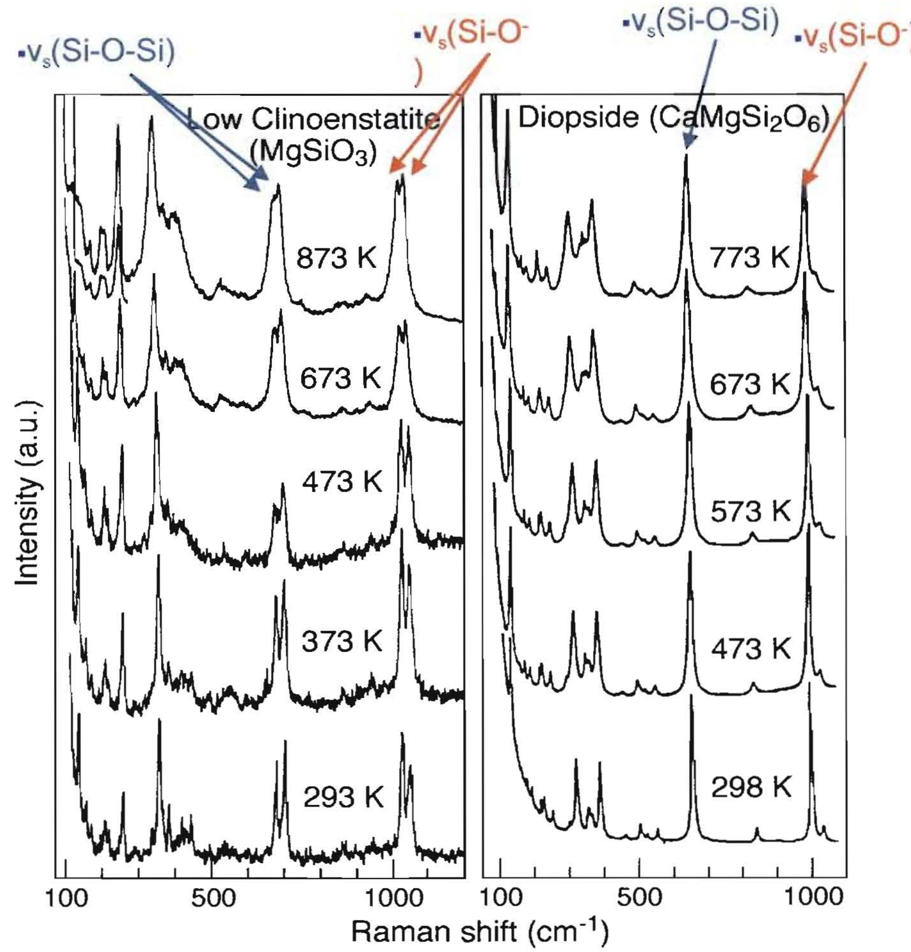
Raman Spectra of Olivine





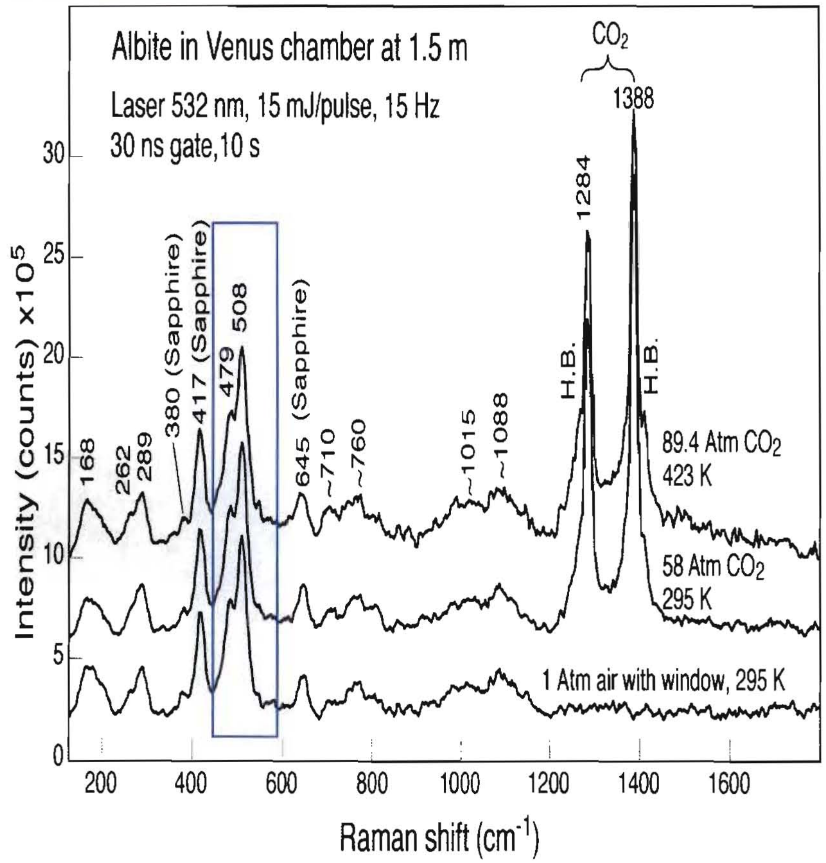
Raman Spectra of Pyroxenes

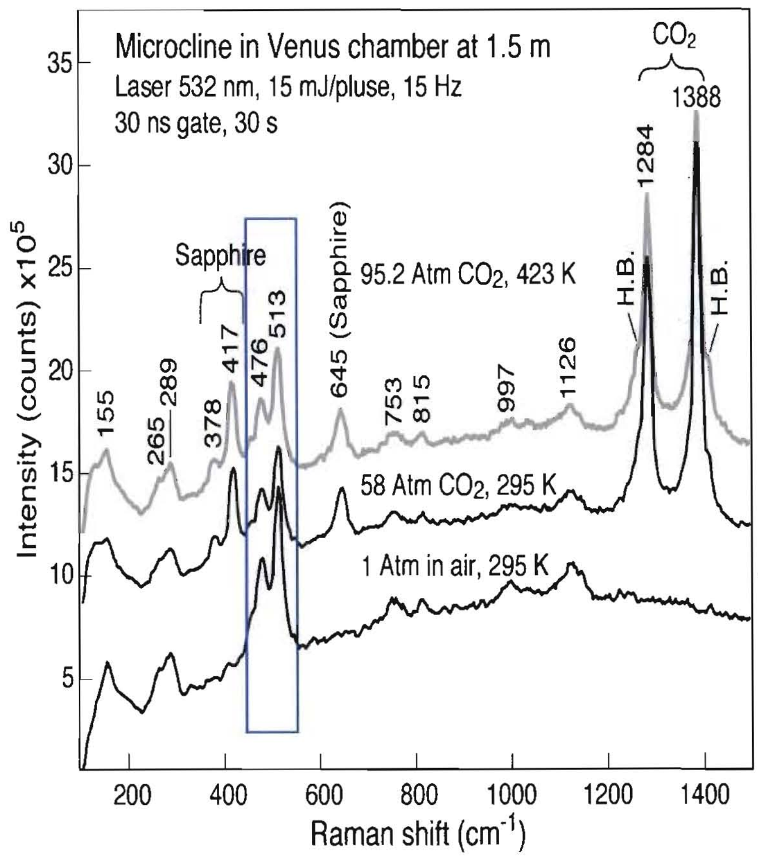




•At 1 Atm in air

Raman Spectra of Feldspar

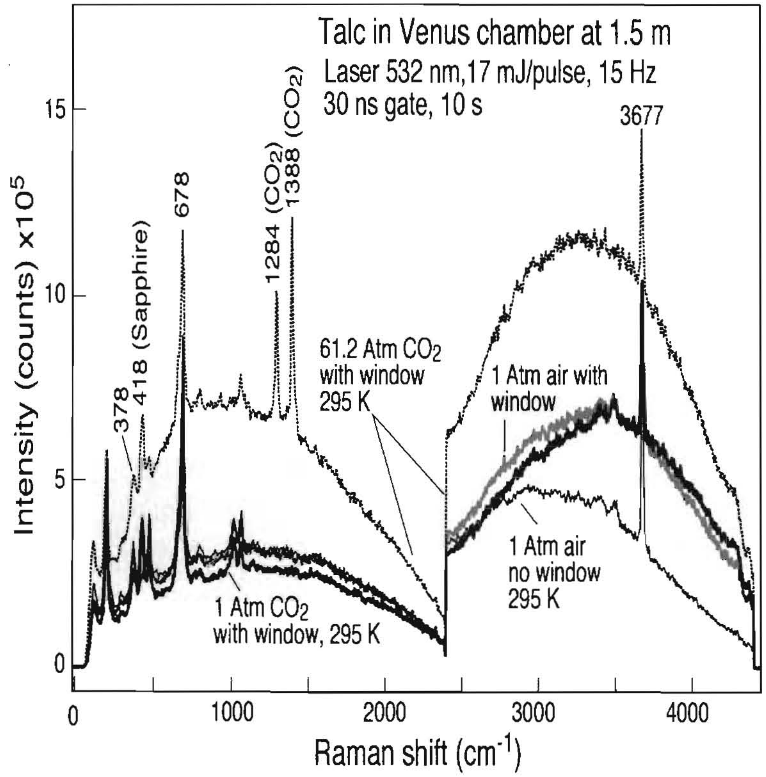


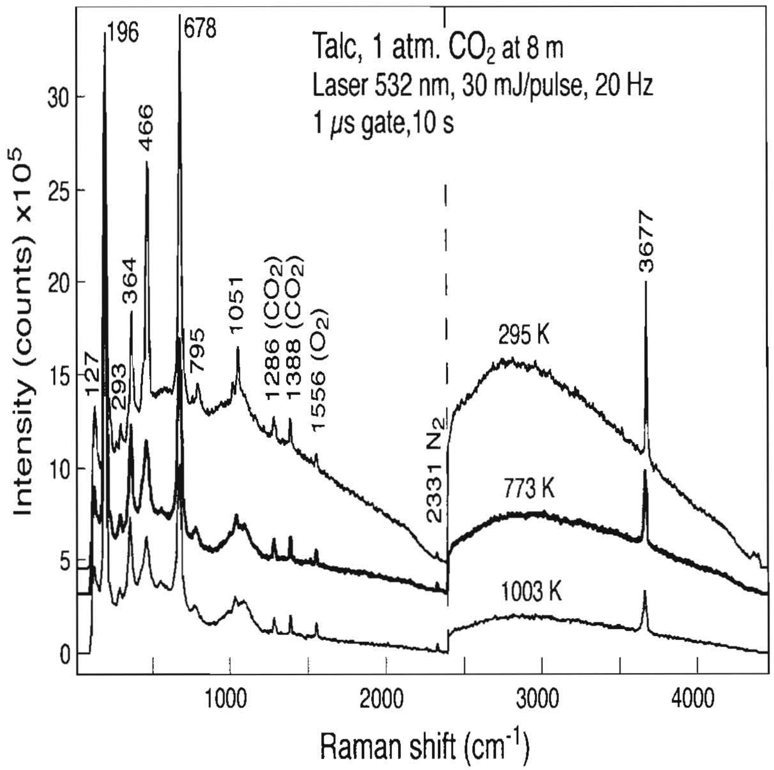


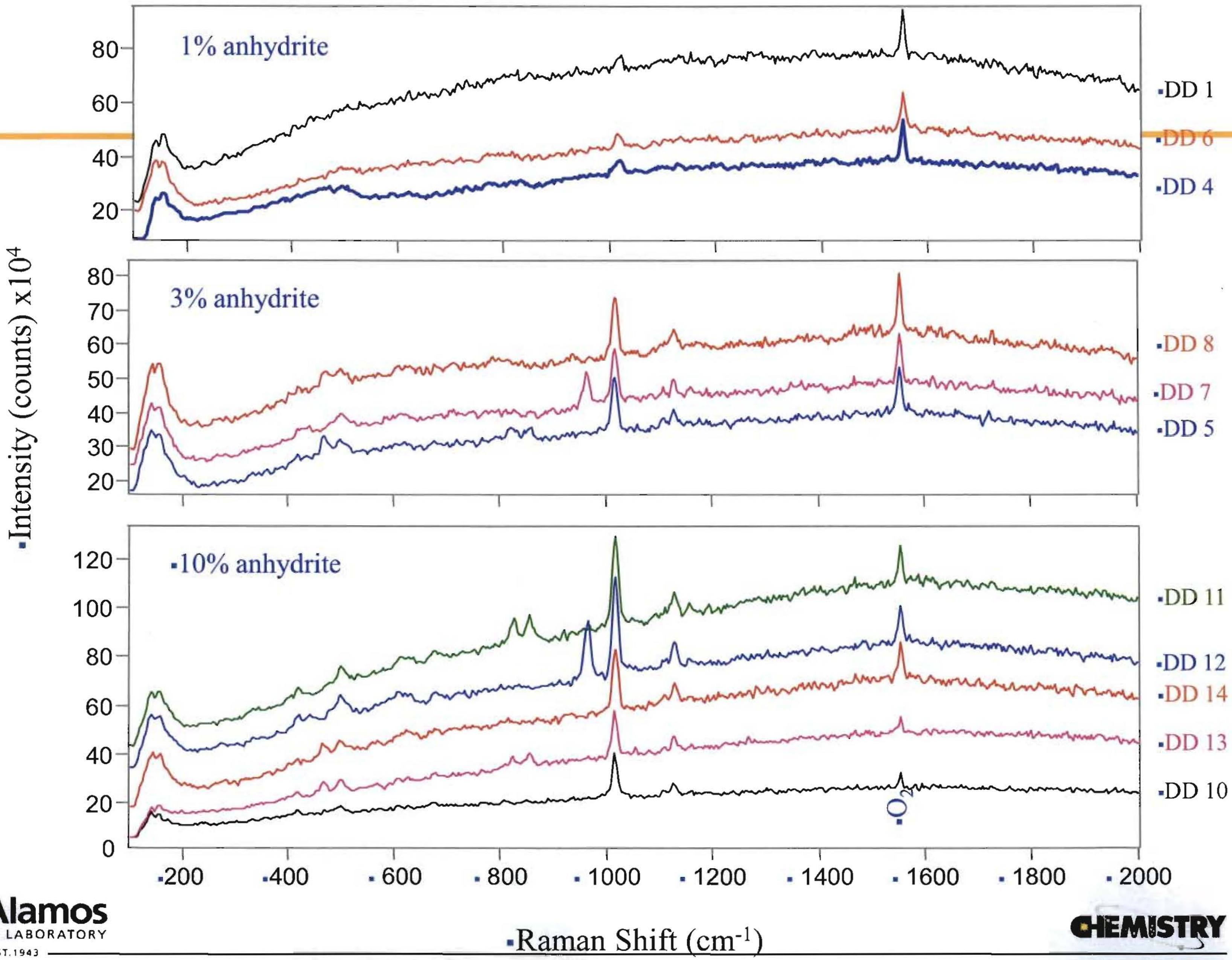
Albite ($NaAlSi_3O_8$): Raman Fingerprints 468 (sh); 508 (s) cm^{-1}

Microcline (KAlSi3O8): Raman Fingerprints 476 (sh); 513 (s) cm-1

Raman Spectra of Talc ($Mg_3Si_4O_{10}(OH)_2$)

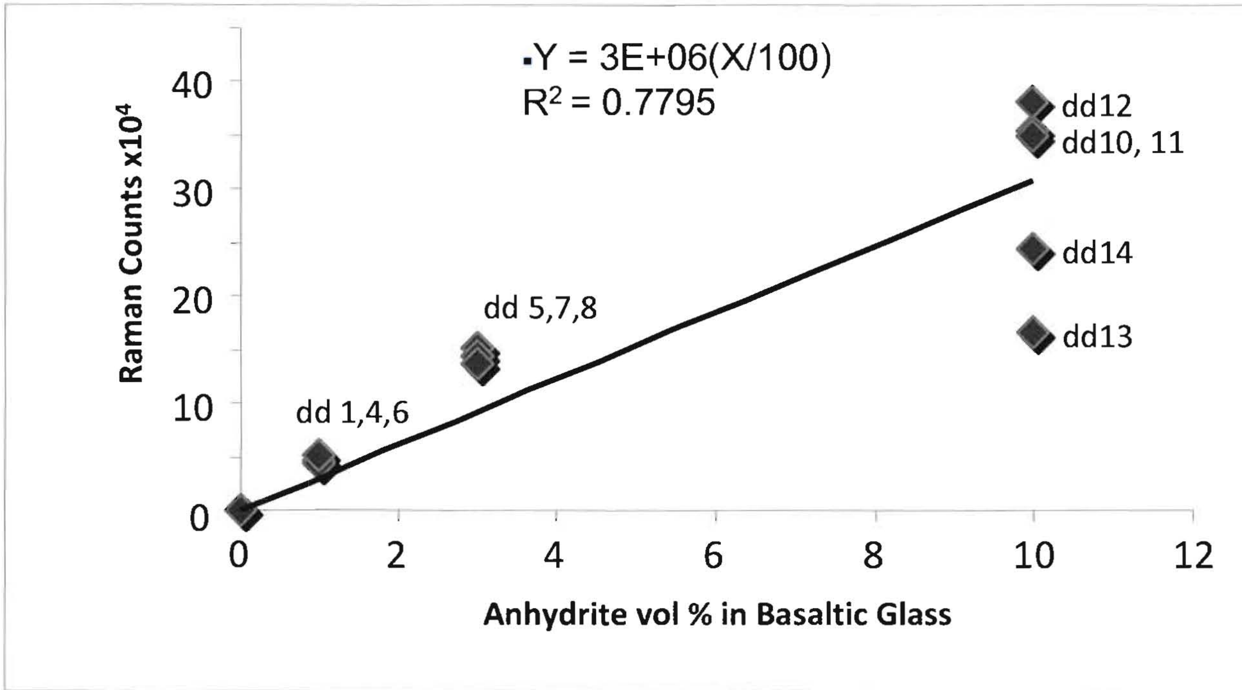




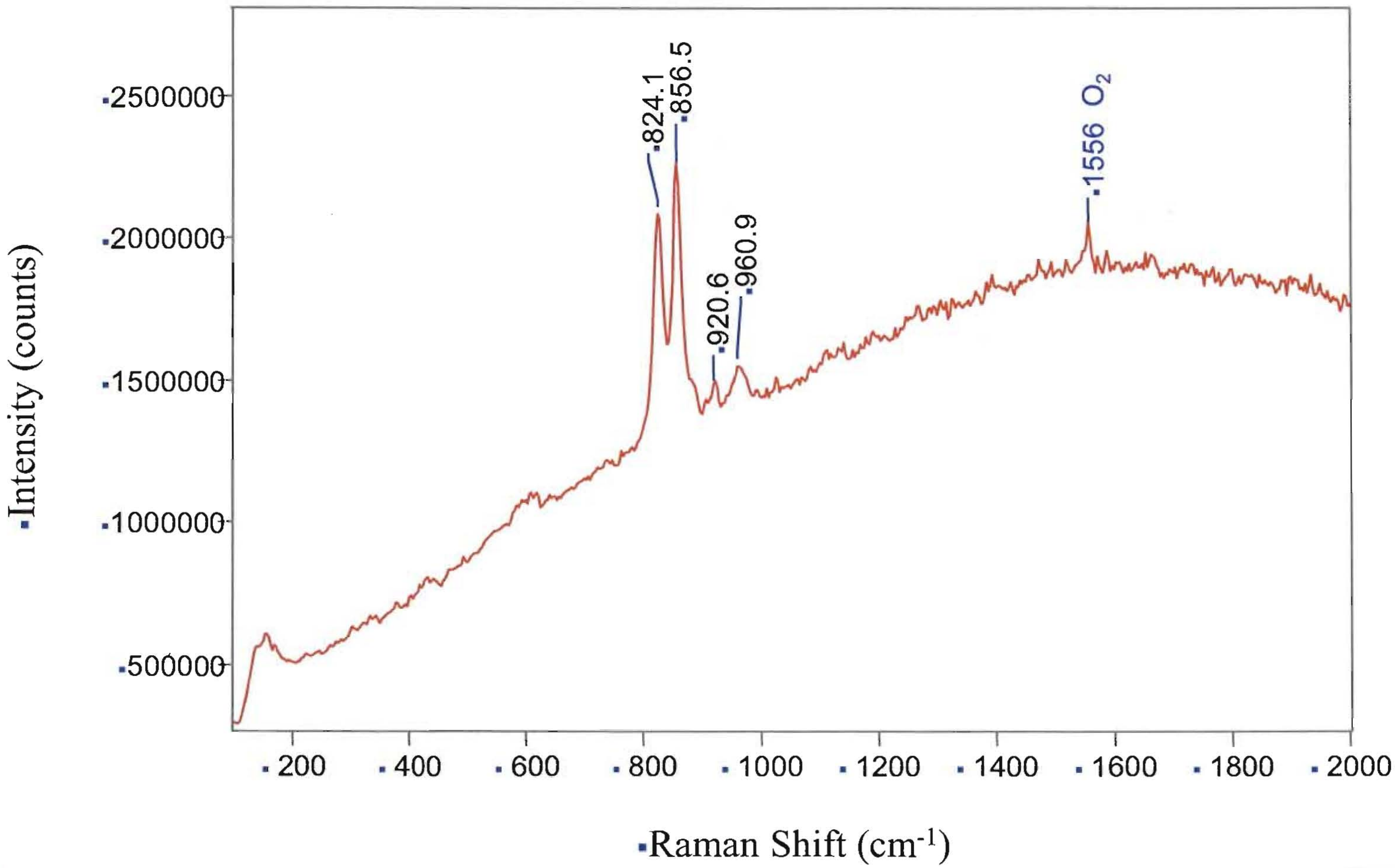


1% anhydrite
3% anhydrite
10% anhydrite
Intensity (counts) x10⁴
Raman Shift (cm⁻¹)
DD 1
DD 6
DD 4
DD 8
DD 7
DD 5
DD 11
DD 12
DD 14
DD 13
DD 10
O₂
80
60
40
20
80
70
60
50
40
30
20
120
100
80
60
40
20
0
200
400
600
800
1000
1200
1400
1600
1800
2000

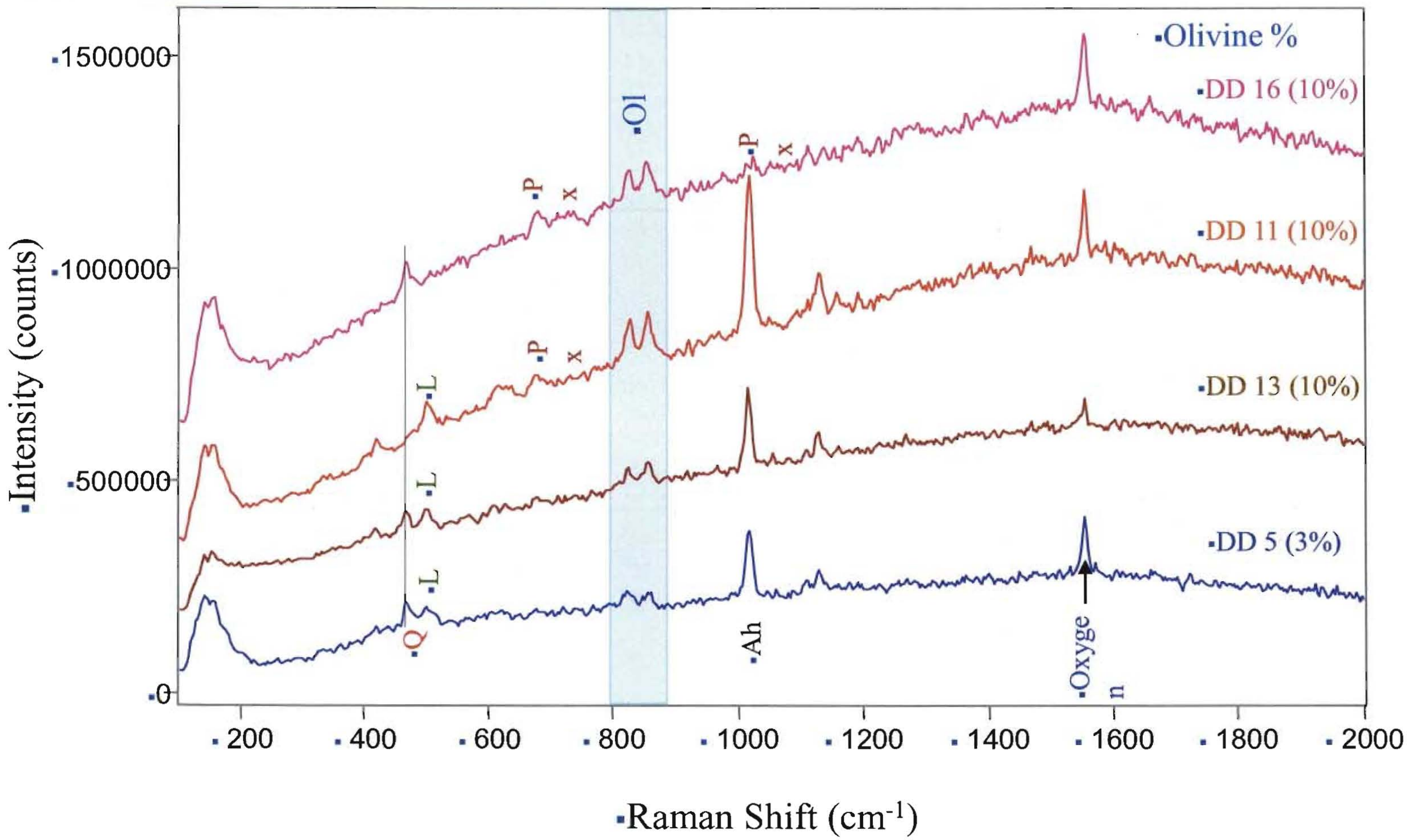
Anhydrite Calibration



Olivine Pressed Powder

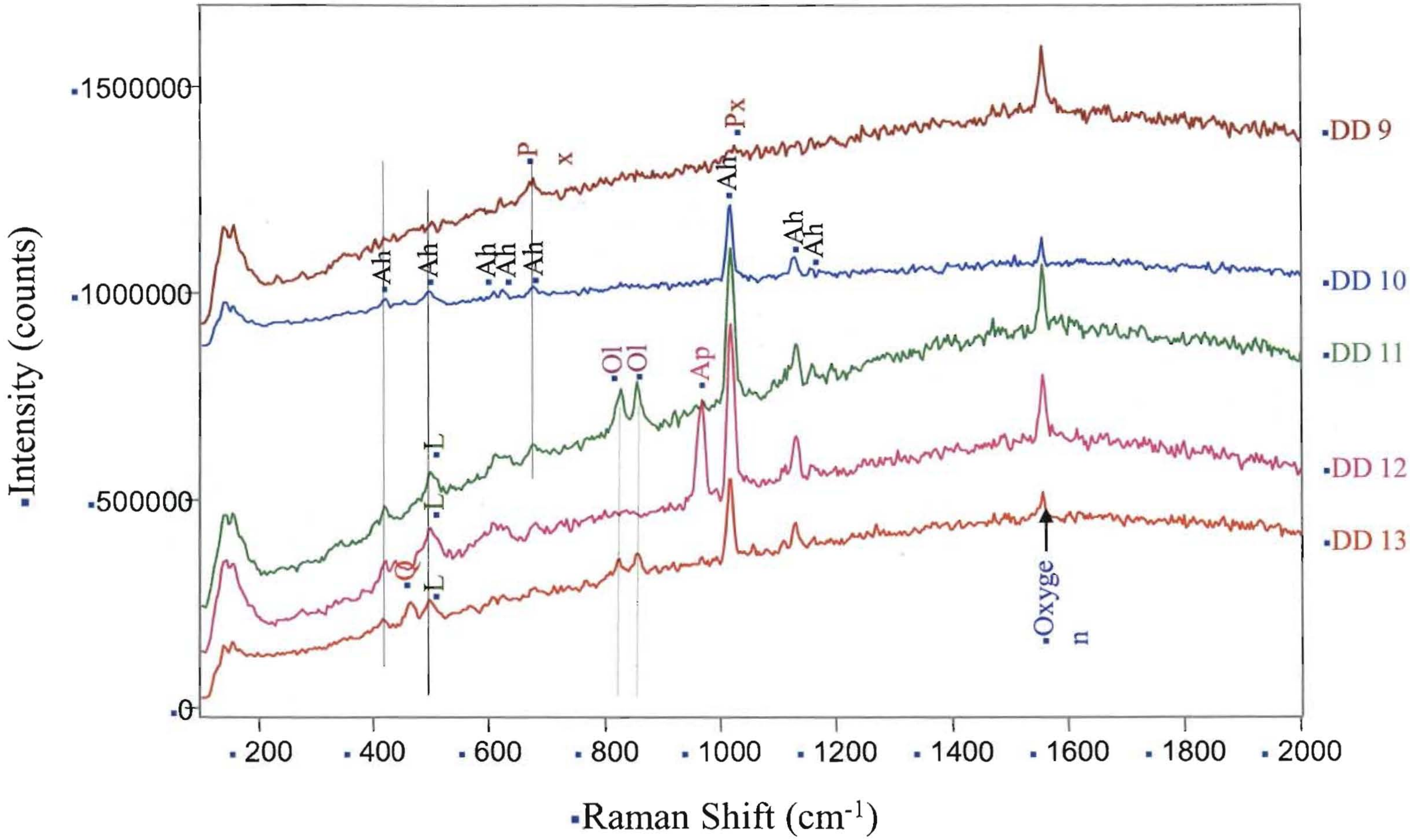


Olivine Containing Mixtures



Ah = Anhydrite; L =Labradorite; Ap = Apatite; Q = α-Quartz; Ol = Olivine; Px = pyroxene

Raman Spectra of Mineral Mixtures



Ah = Anhydrite; L =Labradorite; Ap = Apatite; Q = α-Quartz; Ol = Olivine; Px = pyroxene

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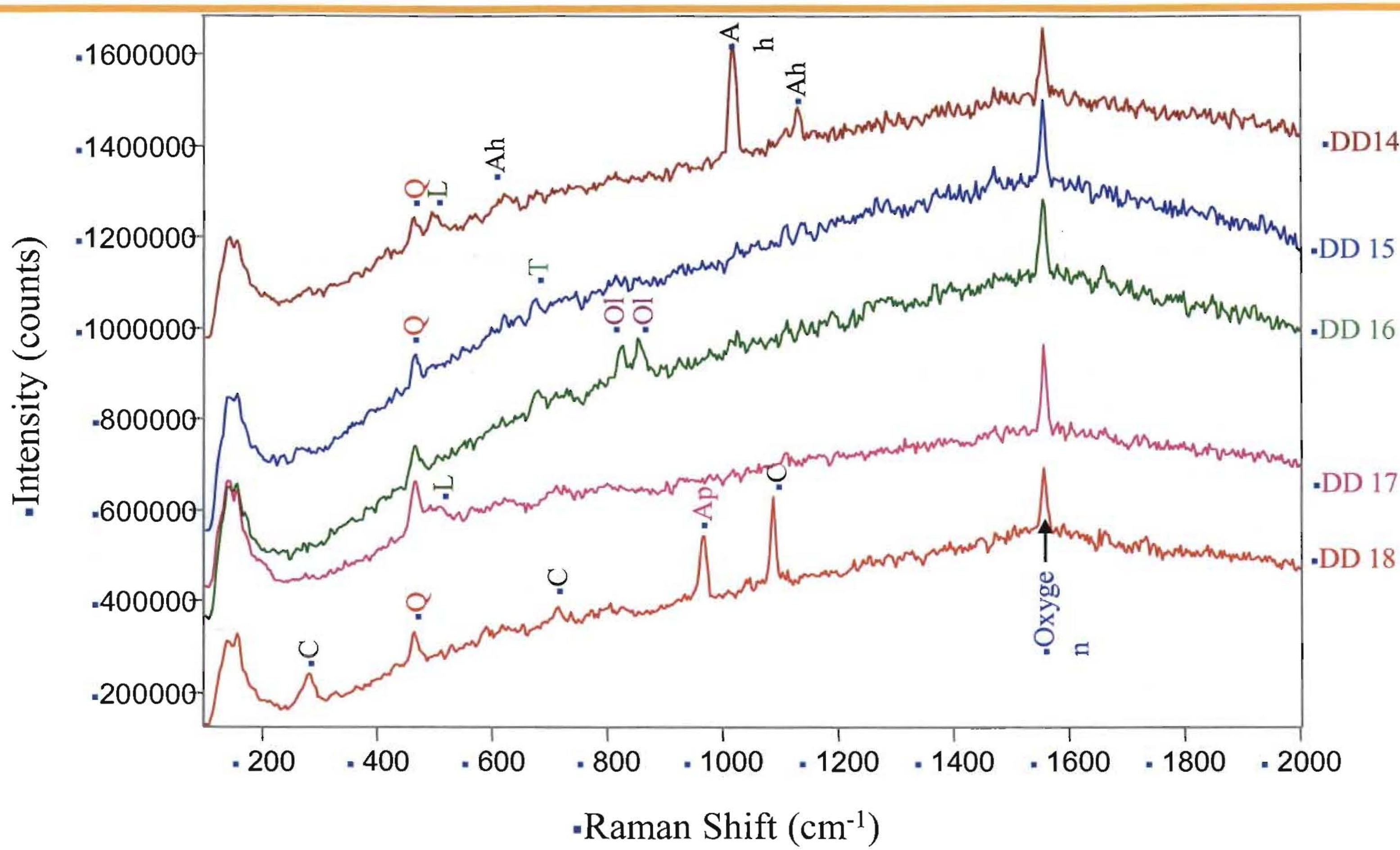


Ah = Anhydrite; L =Labradorite; Ap = Apatite; Q = α-Quartz; Ol = Olivine; C = Calcite; T = Tremolite

Conclusions

- **LIBS (& Raman) are Ideal Remote Technique for Venus Geochemical Exploration**
  - Rapid Quantitative Elemental (& Mineralogical) Analysis
  - No External Arm is Required
  - No Sample Preparation Required
  - Avoids Risks Associated with Sample Collection and Transfer into Lander
- **LIBS Spectra are More Complicated Under Venus Conditions**
  - Than on Earth or Mars
  - Pressure Broadening is Observed
  - Optimal Spectral Resolution needs to be Determined
- **Transmission Through the Thick Atmosphere**
  - Does Not Appear to be a Problem
    - Theoretical Calculations
    - LIBS Spark is Produced and LIBS Emission was Observed.

Thank You

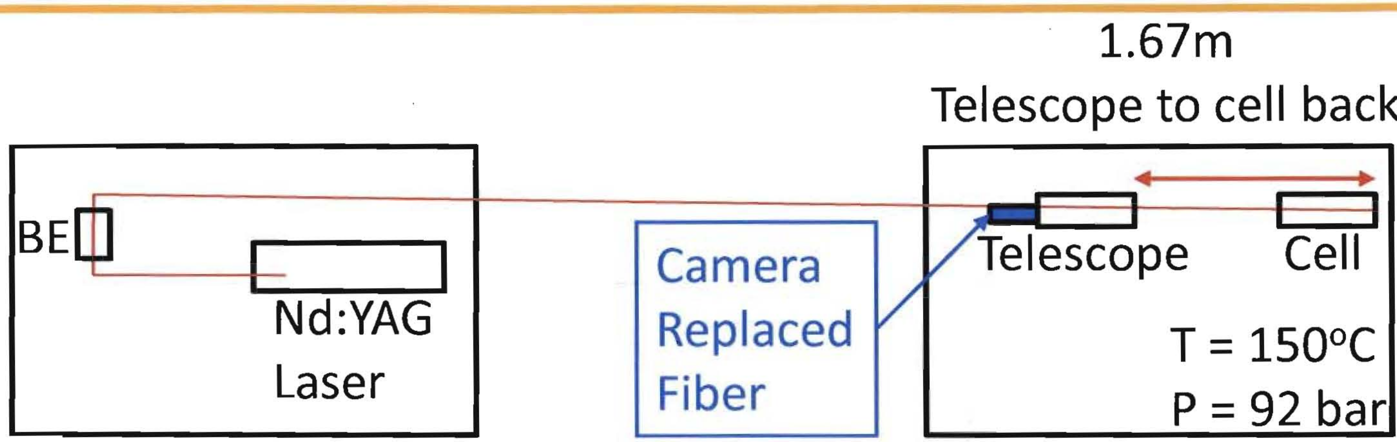
We gratefully acknowledge the Los Alamos National Laboratory (LANL) Laboratory Directed Research and Development (LDRD) Exploratory Research (ER) Program for funding this work.

New Multivariate Analysis Techniques
Partial Least Squares (PLS)

- **Partial Least Squares Regression**
  - Each Spectral Channel is an Independent Variable
  - Each Elemental Composition is a Dependent Variable
  - Pixel – to – Pixel Variations
  - Not Peak Area Analysis
- Model is NOT programmed with Elemental Emission Wavelengths
  - PLS Determines the Correlations Statistically

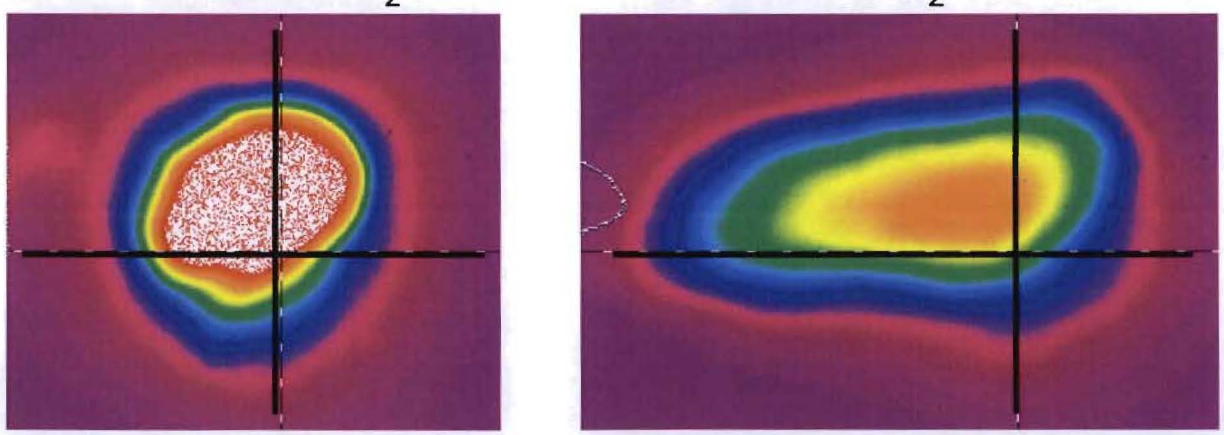
	Elements					LIBS Spectra											
	Si	Ca	Mg	.....	O	λ1 (nm)	λ2 (nm)	λ3 (nm)	λ4 (nm)	λ5 (nm)	λ6 (nm)	λ7 (nm)	λ8 (nm)	λ9 (nm)	λ10 (nm)	......	λ6144 (nm)
Sample 1																	
Sample 2																	
Sample 3																	
Sample 4																	
Sample 5																	
....																	
Sample n																	

Plasma Spot Image

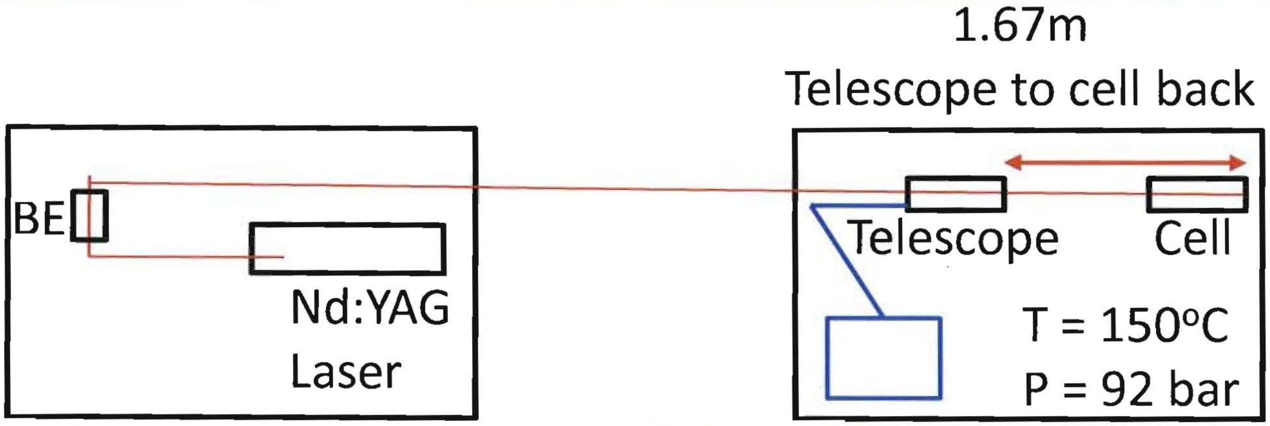


1 laser, single pulse
~50mJ/pulse

1 bar CO_2 92 bar CO_2

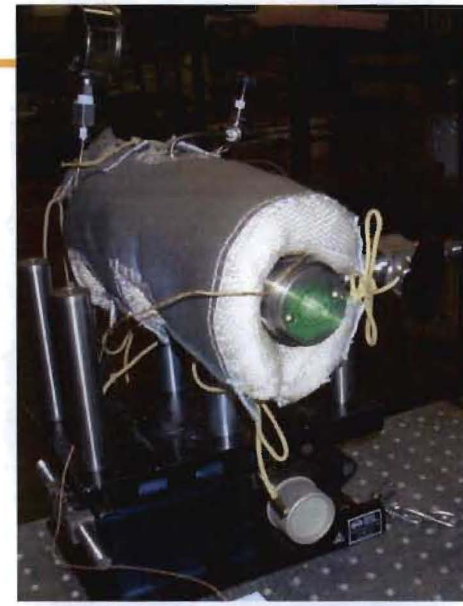


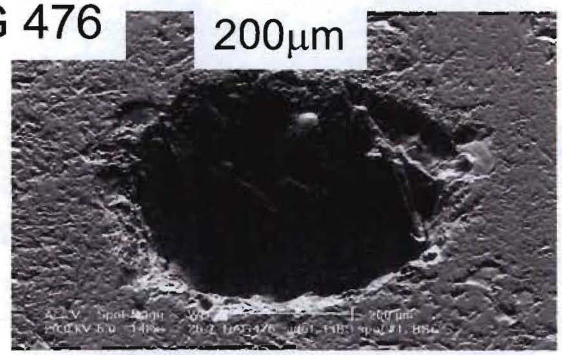
The LIBS Technique



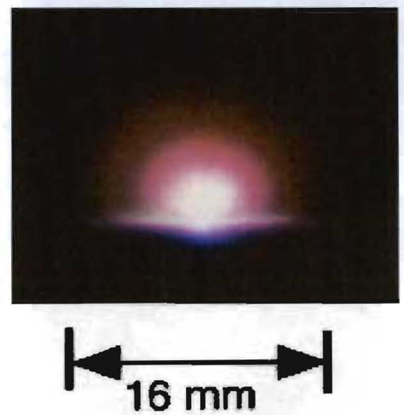
1 laser, single pulse
~50mJ/pulse

Dispersive (240-480nm) and
Transmission (535-800nm)
Spectrometer with ICCD





Thompson et al. JGR-P 111 E05006 2006.



Knight et al. Appl. Spect. 54, 331, 2000.