

RAMAN SPECTROSCOPY OF LOW CONCENTRATION OF MINERALS IN BASALTIC GLASS ANALOG MATRIX APPLICABLE TO PLANETARY EXPLORATION. S. K. Sharma¹, A. K. Misra¹, T. E. Acosta¹, M. D. Dyar², E. A. Speicher², S. M. Clegg³, R. C. Wiens³ and A. H. Treiman⁴, ¹Hawaii Institute of Geophysics and Planetology, University of Hawaii, 1680 East-West Rd., POST #602 Honolulu, HI, 96822 (sksharma@soest.hawaii.edu); ² Dept. of Astronomy, Mt. Holyoke College, South Hadley, MA 01075, ³Los Alamos National Laboratory, P.O. Box 1663 MS J565, Los Alamos, NM 87545; ⁴Lunar and Planetary Institute, 3600 Bay Area Blvd., Houston TX 77058.

Introduction: Raman spectroscopy (RS) has been proposed as a candidate analysis system for missions to Mars and, more recently, as a potential mineralogical analysis system for Venus [e.g., 1,2]. This technique has several distinct advantages over other spectroscopic techniques that have been used on past missions, specifically including the capability for rapid mineralogical analyses at stand-off distances. For planetary applications, the sharpness of the Raman spectral features allows far more definitive detection of minerals, especially in mixtures. Detection of bulk minerals under simulated Venus conditions has been demonstrated utilizing stand-off Raman system [e.g., 3,4]. In this paper, we characterize Raman spectra of seven mineral species suggested to be present on Venus, and examine detection limits in mixtures with a basaltic glass analog that strongly absorbs in the visible radiation including the 532 nm laser beam that was used in this study for Raman excitation.

Samples: Starting samples were chosen based on work that builds upon results from the Vega and Venera landers. Those three sets of XRF major element analyses from the surface of Venus all suggest the presence of basaltic rock types along with variable amounts of S, either primary or secondary from atmospheric interactions. The most common models predict that the surface of Venus is rich in the mineral wollastonite or the assemblage calcite + quartz, depending on elevation and temperature [e.g., 5-8]. These models also predict that the iron minerals hematite or magnetite will be present. Other workers [9-11] used thermochemical modeling to predict chemical weathering reactions between basalt and a CO₂ and SO₂-rich atmosphere. Depending on the starting materials and reaction length scales, they predicted that the weathering products would include anhydrite, feldspar, andalusite, cordierite, quartz, hematite, and/or magnetite.

Other predictions of Venus surface mineralogy come from Burns and Straub [12-13], who used observed emissivity to infer the presence of magnetite, hematite, Fe-sulfides, olivine, amphibole, micas, and ilvaite.

From these models, we selected a set of seven minerals for use in creating fine-grained mechanical mixtures of varying amounts of minerals and glasses likely to be present on Venus surface (Table 1). We then

created mixtures of these rocks with a synthetic Fe-containing glass, using 1, 3, and 10 % by volume of each mineral. Fine grain mixtures of glass and various minerals were pressed to form a 12.5 mm disk and used for Raman measurements.

Table 1. Samples Studied							
Minerals Used in Mixtures							
Anh	Anhydrite (sulfate)						
Px	Diopside (pyroxene)						
Ap	Chlorapatite (phosphate)						
Lab	Labradorite/anorthite (plagioclase)						
Ol	Forsterite (olivine)						
Qtz	α -Quartz (oxide)						
Cal	Calcite (carbonate)						
Mixtures (% are by mineral mode, or vol. %)							
	Anh	Px	Ap	Lab	Ol	Qtz	Cal
DD1	1	1		1	1	1	
DD2		3					
DD3		1					
DD4	1			1		1	
DD5	3	3		3	3	3	
DD6	1		1	1			
DD7	3		3	3			
DD8	3			3			3
DD9		10					
DD10	10	10					
DD11	10	10		10	10		
DD12	10		10	10			
DD13	10	10		10	10	10	
DD14	10			10		10	
DD15						10	
DD16		10			10	10	
DD17				10		10	
DD18			10			10	10
D.L.*	1	10	1	3	1	1	1

*D.L. = Detection limit in glass matrix

Experimental Setup: Raman experiments employed a Nd:YAG frequency doubled pulse laser operating at 10 Hz and with a maximum pulse energy of 17 mJ/pulse at 532nm. The pulse width of the laser pulses was 10 ns. A 10x beam expander was used to

focus the 532 nm laser beams to 5-mm diameter spot onto the sample.

A stand-off Raman collection system described in earlier publications [3,4] was used for observing the scattered light from the samples located at a distance of 2-m from the system in the air. The scattered light was analyzed with an intensified CCD detector operated in the gated mode. Raman spectra were collected from the samples with 100-ns gate.

Results: Figure 1 shows the Raman spectra of the glasses containing 3 to 10% of olivine with other minerals as listed in Table 1. Raman fingerprints of olivine at 824 and 855 cm^{-1} and atmospheric oxygen at 1556 cm^{-1} over the fluorescence background in the glasses containing 3% to 10% by volume are clearly visible in the spectra (Fig. 1). The Raman fingerprint of anhydrite at 1018 cm^{-1} produces a strong Raman line in DD5 containing 3% by volume of anhydrite in the glass matrix. Raman fingerprints of quartz at 466 cm^{-1} and of labradorite consisting of a doublet at 482 and 508 cm^{-1} are also detected (Fig. 1). Pyroxene diop-

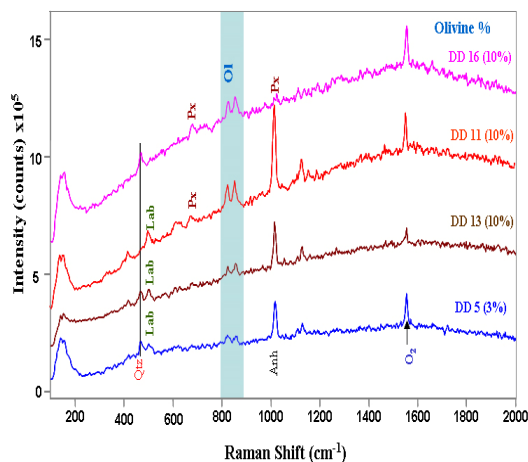


Fig. 1. Remote Raman spectra of minerals in basaltic glass matrix (Laser 532nm, 10 ns, 17mJ/pulse, 15 Hz; integration time 30 s).

side has relatively weak lines at 666 and 1013 cm^{-1} and is only detectable in the glass spectra containing 10% of pyroxene. In the sample containing anhydrite, the 1013 cm^{-1} Raman line of the Px is partially masked by the strong line of anhydrite at 1018 cm^{-1} . In the spectra of DD8 containing 3% by volume calcite, a strong Raman line of symmetrical stretching mode of carbonate at 1084 cm^{-1} is detected (not shown in Fig. 1).

Detection Limits: One of the goals of this project was to determine detection limits for various minerals in a glass matrix, analogous to phenocrysts in a magma or alteration materials mixed into a weathered rock. The detection limits for each phase are given in the bottom row in Table 1. The relative Raman efficiencies of the various minerals vary with mineral species

[14], and also show dependence on grain orientation [15] and particle size [16]. The basaltic analog glass used in the present study show strong absorption of the laser beam. We found that the depth of penetration of the 532 nm beam was <15 micrometer in the glass. The measured remote-Raman spectra are, therefore, of the mixed minerals close to the surface of the glass samples.

Summary: The Raman data presented here show the ability of the gated stand-off Raman system with pulse laser excitation to detect low concentrations of mixed minerals in strongly absorbing matrix such as basaltic glass. The technique would be ideal for identifying minerals on a planetary surface during daylight and nighttime. The proposed stand-off Raman spectrometer for the SAGE Venus mission will be able to detect Raman fingerprints of mixed minerals with moderate to high relative Raman cross section on the Venus surface. A gated stand-off Raman spectrometer will also be very useful for future Mars missions such as the Mars Astrobiology Explorer-Cacher (MAX-C) rover [17] proposed to be launched in 2018 together with the European ExoMars rover.

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