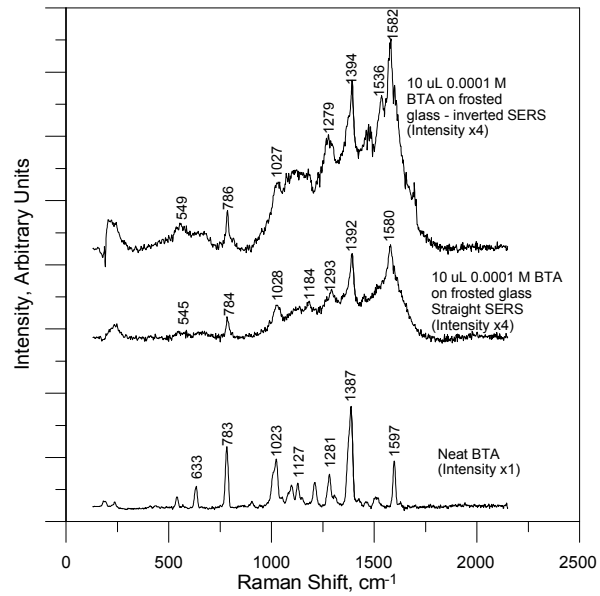
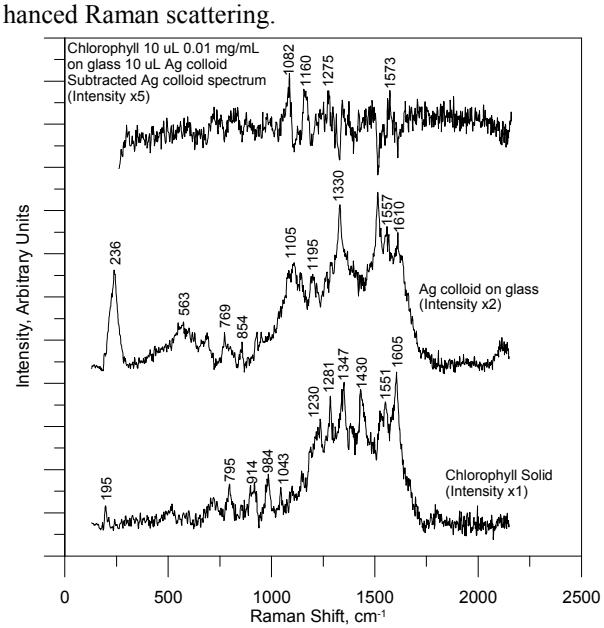
DEVELOPMENT OF A SURFACE ENHANCED RAMAN SPECTROSCOPY TECHNIQUE FOR IDENTIFICATION OF BIOMARKERS ON MARS N. Sridhar[1], D.S. Dunn[1], K. T. Price[1], M.A. Miller[1], R.T. Pabalan[1] and T.A. Abrajano[2], [1]Southwest Research, 6220 Culebra road, San Antonio, Texas, 78238, (E-mail of corresponding Author: nsridhar@swri.org) , [2]Department of Earth and Environmental Sciences, Science Center, Room 2C04, Rensselaer Polytechnic Institute, 110 8th Street, Troy, NY 12180-3590

Introduction: One of the most important goals for the Mars missions is obtaining evidence of past or present life. In-situ analyses using a suite of on-board instruments on a number of small, scout missions to Mars are envisaged prior to more detailed sample return missions. There is a keen interest in Raman spectroscopy as an *in-situ* analytical tool because of the possibility of obtaining molecular and mineralogical information. The main limitations of Raman spectroscopy are its inherently low intensity compared to the elastically scattered laser intensity and interference from fluorescence due to the electronic excitation of the molecule by the laser. Analysis of biomarkers indicative of life on Mars will require higher sensitivity and signal to noise ratio than normal Raman spectroscopy can offer. Surface Enhanced Raman Spectroscopy (SERS) is a phenomenon whereby the Raman intensity is increased by as much as a million fold due to the presence of nano-size silver or other appropriate metal particles on the surface to be analyzed [1,2]. Therefore, SERS technique may be useful for analyzing small concentrations of biomarkers in the Mars soil or minerals. SERS requires extremely close proximity of the molecule to be analyzed to the metal particles that form the SERS substrate. Such close proximity is difficult to achieve for solid phase. An "inverted" SERS technique is demonstrated where SERS-sensitive metal nanoparticles are deposited on the material to be analyzed.

Demonstration of Inverted SERS Technique: We used Benzotriazole as a probe molecule and showed that the detection limit was less than 1 femtomole (10^{-15} moles). SERS was effective in detecting small concentrations of organic molecules on naturally occurring minerals, such as quartz (Figure 1). In this method, the colloidal silver was deposited from an aqueous phase [3]. A comparison to the typical method of performing SERS (i.e. depositing the analyte on top of a SERS substrate) is shown in Figure 1. Chlorophyll, used as an analog of a biomarker molecule that could be present in small concentrations on Martian soil or subsurface, yielded Raman spectrum at concentrations as low as 78 femtomoles (Figure 2). Degradation of such molecules under 532 nm laser light was significant. SERS is especially useful in this regard because the time exposure and laser power needed for analysis can be reduced. Such a technique was also effective in detecting small concentrations of a powdered mineral mixed with a large concentration of another mineral (e.g., powdered pyrite mixed with silica powder). Minerals, such as zeolites, where ion-exchange reactions occur between sodium and silver, also showed enhanced Raman scattering.





Investigation of Biomarker Molecules:

Our effort to evaluate the application of inverted SERS on potential Mars biomarkers considers both the target biomolecules/residue and likely mineral substrates. The latter includes oxides/oxyhydroxides (e.g., hematite, goethite), silicates/hydrated silicates (e.g., smectite, palagonite), sulfate (e.g., jarosite) and carbonates (e.g., magnesite). Potential biomarkers consist of both original biomolecules and likely alteration products. Original biomolecules include lipids (e.g., fatty acids, carotenoids, amino acids) and weathering products such as salts of labile organic acids (e.g., benzoic acid, carboxylic acids, benzenehexacarboxylic acids) and weathering residues (e.g., PAHs, kerogen, graphite). These weathering products are expected to result from the interaction of the original biomolecules with UV radiation and potent oxidants on the Martian surface [e.g., 4].

References: [1] Moskovits, M. (1985). *Review of Modern Physics.* 57 (3). 783-826. [2] Norrod, K.L., L.M. Sudnik, D. Rousell, and K.L. Rowlen. (1997). *Applied Spectroscopy*. 51 (7). 994-1001. [3] Yang J., and S.-H. Chen, (2001), *Applied Spectroscopy* 55 (4): 399-406. [4] Benner, S.A., Devine, K.G., Matveeva, L.N. and Powell, D.H. (2000), Proc. Nat. Acad. Sci. 97 (6) 2425-2430.