CRITICAL ASSESSMENT OF BIOSIGNATURE DETECTION WITH RAMAN SPECTROSCOPY ON BIOLOGICALLY LEAN SOILS. M.B. Wilhelm[1,2], A. Sansano[3], J.A. Sanz-Arranz[3], P. Sobron[4], F. Rull[3], A.F. Davila[1], [1]Space Science & Astrobiology Division, NASA Ames Research Center, Moffett Field CA 94035 (marybeth.wilhelm@nasa.gov), [2]Georgia Institute of Technology, [3]Unidad Asociada UVA-CSIC Centro de Astrobiología, [4]SETI Institute

Introduction: The Mars2020 and ExoMars rovers will each carry a Raman Spectrometer to Mars to identify and characterize minerals, organic compounds and biomarkers. The Raman Spectrometer was selected in part due to its operational simplicity—it analyzes samples at a distance, non-destructively and with minimal or no sample handling. However, operational simplicity comes at a performance cost, and the limit of detection (LOD) of the Raman Spectrometer will be lower than other analytical systems such as GC/MS. We undertook a project to critically evaluate the capability of the Raman Spectrometer to detect organic compounds and biomarkers in organically and biologically lean natural samples from the Atacama Desert.

Raman library and natural samples: First, we built a Raman spectral library of hydrocarbons and lipid biomarkers using analytical standards. Analytical standards were analyzed with three different Raman Spectrometers (532nm, and 1064nm-FT-Raman) to get the best spectra as possible. Analyzed standards included short-chain and cyclic hydrocarbons expected on Mars from abiotic sources, as well as the main classes of lipids biomarkers found in Atacama soils and other natural samples. We also selected a suite of Atacama soils samples with one of the lowest biomass contents anywhere on Earth, assumed to be a "best case scenario" for samples containing evidence of life on Mars. Lipid biomarkers (~ppb concentrations), amino acids (ppb), and proteins/peptides (ppm) have been thoroughly characterized in these samples in the laboratory [1], and as such, these samples provide an excellent baseline to test flight unit performance.

Analyses with the ExoMars flight prototype: To be as mission relevant as possible, Atacama soil samples were be analyzed using the same protocols planned for the ExoMars mission. We used the ExoMars RLS Simulator at UVa-CSIC-CAB Associated Unit. This Simulator allows to perform several scientific key experiments under conditions similar to those of the RLS on the ExoMars rover. It also provides the means for the definition and development of the necessary algorithms for the automation of the instrument measurements [2]. Powdered soil samples were placed on a refillable container similar to ExoMars' sample distribution carousel serving the RLS, which can be emptied and reused for new analyses just as during mission operations. The RLS, in its automatic mode, then analyzed a set of at least 10 points in each sample, with a 50 microns spot size and an irradiance level of 0.6–1.2 kW cm–2 with a 532 nm continuous wave (CW) laser [3].

Results: Biomarker standards of interest for astrobiology, such as lipid and hydrocarbon biomarkers, have distinct Raman spectra that can be used as diagnostic for the presence of these compounds in natural samples. The ExoMars RLS Simulator instrument detected organic carbon (only C-C bonds) in soil samples from the hyperarid core of the Atacama Desert (Fig. 1), including a stratigraphic sequence that reflects a change in environmental conditions from wet-to-dry. However, the Raman instrument failed to identify the most abundant lipid and hydrocarbon biomarkers (e.g. C16:0 and C18:0 fatty acids) known to be present in the same soil samples at ppb concentrations

Preliminary conclusion: Raman spectroscopy could be a suitable (relatively simple operations, no sample contact, no sample prep…) diagnostic tool for the presence of organic compounds in natural samples. However, current prototypes might not be capable of detecting biomarkers present in complex natural samples (soils, sediments, regolith…) if present at concentrations equivalent or lower to the biologically leanest environments on Earth.

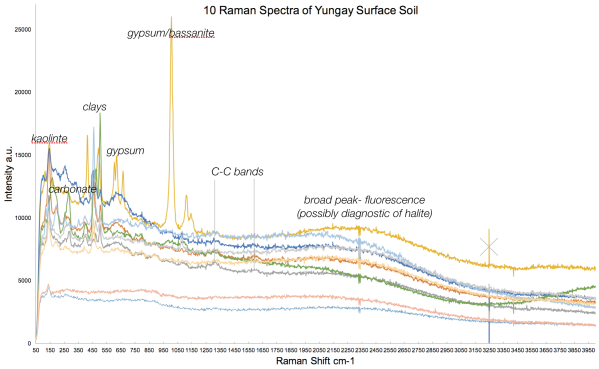

Figure 1. Data from ExoMars RLS Simulator, 10 random points on bulk soil from the Atacama Desert. Spectra yielded a good mineralogical snapshot. Organic carbon (C-C bonds only) was detected in about half of the spectra collected. No specific biomarkers were observed.

References:

[1] Wilhelm M.B. et al., (2017) *Org Geo, 103,* 97-104. [2] Lopez-Reyes, G., et al. (2013). European Journal of Mineralogy 25 (5): 721–33. [3] Rull, F., et al. (2011). ExoMars Raman Laser Spectrometer for ExoMars.