

**TERRESTRIAL ROCK VARNISH: IMPLICATIONS FOR BIOSIGNATURES ON MARS.** C. Yeager<sup>1</sup>, N. Lanza<sup>1</sup>, R. Marti-Arbona<sup>1</sup>, M. Teshima<sup>1</sup>, U. Lingappa<sup>2</sup>, W. Fischer<sup>2</sup>, <sup>1</sup>Los Alamos National Laboratory (cyeager@lanl.gov), <sup>2</sup>California Institute of Technology.

**Introduction:** On Earth, there is a close association between Mn deposits and the presence of Mn- and Fe-oxidizing microbes [1,2]; as such, Mn is considered a principal biosignature for Mars [3]. The most common terrestrial Mn-rich surface material on Earth is desert varnish, a dark, shiny coating on rocks in arid locations. Microbes occupy crevices, pores and layers within rock varnish, and it is probable that the concentration of Mn in many rock varnishes is mediated by microbial activity; however, the relationship between microbes and varnish remains a source of long-standing controversy [4].

Here we report research aimed at 1) identifying and interpreting the microbial species and processes involved in the habitation and/or formation of rock varnish, and 2) identification of organic biosignatures that, in concert with trace element and mineralogy, can be used to conclusively distinguish the biogenic and abiogenic origins of terrestrial Mn-rich surfaces so that we may then apply the knowledge gained in this work to current and future Mars mission datasets, including ChemCam and SuperCam.

**Approach:**

Microbial communities associated with rock varnish were examined from samples collected throughout southwest U.S. by analysis of both targeted 16S rRNA (bacteria, archaea) and ITS (fungi) sequence libraries and shotgun metagenomic libraries. We also seek to identify unique and/or important organic biosignatures present in varnish.

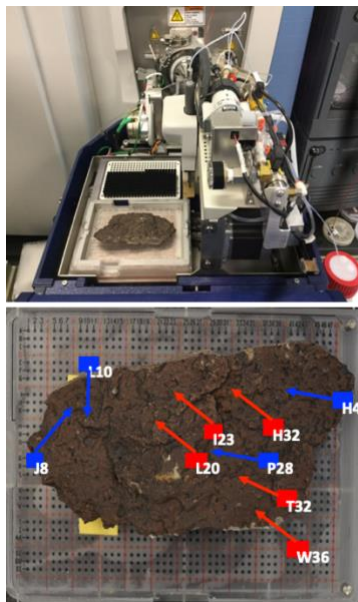


Figure 1. A) LESA LC-MS system to analyze biosignatures at B) the millimeter-scale on varnished rock

Preliminary work has been done to chemically characterize organic materials extracted from rock varnish samples using LC- and GC-MS (Figure 1) and

GC-FT-IR to obtain differentiating information about molecular chemical bonds. In addition, we plan to analyze rock varnish samples with Raman and LIBS to obtain chemistry and mineralogy data that is equivalent to ChemCam and the upcoming SuperCam. Being able to compare the molecular signatures (MS and differentiated by IR) of the extracted samples to intact samples will create a signature database that will directly link IR features (ChemCam & SuperCam) to specific molecular structures and terrestrial biosignatures.

**Results:** Microbial communities inhabiting varnish were shaped by both location (larger contribution) and rock type. The varnish environment selects for a core group of UV- and desiccation-tolerant microorganisms, including bacterial (*Rubrobacteraceae*, *Xenococcaceae*, *Sporichthyaceae*, *Sphingomonadaceae*) and fungal (*Lecanoromycetes*, *Dothideomycetes*) taxa, across landscapes and rock types. Initial LC-MS analysis of 30 spots on the surface of a single varnished rock yielded 3,878 features and ~2,500 metabolites. Examples of metabolites linked to biological pathways that were identified on the surface of the rock include: a) glutathione disulfide, a key metabolite for desiccation resistance in fungi and bacteria, b) organic acids, which are key metal chelators and weathering agents produced by microbes, and c) a variety of amino acids.

**Implications:** We have found that a core group of microorganisms inhabit rock varnish across the southwest U.S. and that we can detect and identify hundreds to thousands of metabolites/proteins on the surface of varnished rocks. Moving forward we will further examine the microbial role in processes involved in rock varnish formation and perform a systematic, spatial proteomics/metabolomics analysis of the surface and interior of key rock varnish samples (e.g., in crevices, varnish surface, near/far from visible fungi or lichens, etc.) and integrate with metagenomic data. In tandem with elemental and mineralogical analysis, we then aim to discover biosignatures that could be identified associated with Mn-rich rocks on Mars using ChemCam or SuperCam.

**References:** [1] Dorn R. I. and Oberlander T. M. (1982) *Prog Phys Geogr*, 6, 317-367. [2] Tebo B. M. et al. (2005) *Trends Microbiol*, 13, 421-428. [3] Lanza N. L. et al. (2014) *Geophys Res Lett*, 41, 5755-5763. [4] Goldsmith, Y. et al. (2014) *Geochim. Cosmochim. Acta*, 126, 97-111.