Spectral Characterization of Endolithic Communities with Reflectance and Raman Techniques. W. M. Calvin[1], L. M. LaCroix[1], and H. Sun[2], [1]Geological Sci. & Eng. University of Nevada, Reno, NV (wcalvin@unr.edu), [2]Desert Research Institute, Las Vegas, NV (Henry.Sun@dri.edu).

Introduction: Infrared spectroscopy has long been used to identify organic molecules [e.g. 1,2]. In particular, biological pigments (chlorophyll, carotenes) cause unique absorption features in the visible and bonds between carbon, nitrogen, sulfur and hydrogen and oxygen have well-known features in the infrared. Of interest in planetary exploration is that features attributed to organic materials overlap with those of common rock and inorganic surface materials [e.g. 2-4]. While some planetary surface environments may destroy organic substances, we continue to look for these materials throughout the solar system and spectroscopic techniques are the mainstay of mineralogical and chemical remote and in-situ identifications. The development of highly portable field instruments now allows their deployment in a host of field settings on Earth. This effort is focused on unraveling the complicated spectral signatures of microbial communities that grow on or in host rocks in an effort to assist rapid field identifications and potential future in-situ applications on Mars.

Samples: We have collected a range of microbially colonized rocks from harsh environments, similar to those identified by Dong et al. [5]. These include six endoliths in granite, sandstone, gypsum, and halite, two hypoliths in quartz/chalcedony, a cryptogamic soil crust, and an epilith on granite. They were collected in the Mojave, Atacama, Utah, and New Mexico deserts, and in Antarctica. We are interested in establishing the spectral features of different community types, to see how similar or different they are from each other. We also want to explore whether a particular type of host rock is more conducive to identification of biologic communities, or if containment in a particular host rock obscures more of the biological signature. Figure 1 shows typical endolithic communities collected in the Atacama.

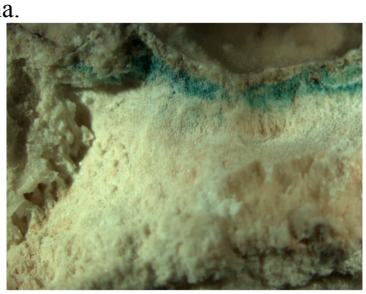

Figure 1: Endolithic communities (green) in salt crust from the Atacama.

Methods: Our measurements include spectral characterization using passive reflectance, active FTIR reflectance and Raman. This incorporates both the wavelength range of significant, known absorption features as well as recent developments in Raman. Passive (solar) reflectance has been used to identify materials on every planet and satellite in the solar system, while active FTIR reflectance accesses longer wavelengths and has been proposed for in-situ investigation on Mars. Raman spectroscopy has recently been used to identify individual bacteria and other microorganisms, and is sensitive to organic constituents. Systems for use in planetary exploration have been developed and successfully deployed in the field and Raman+LIBS is slated for the ESA mission ExoMars [6].

Our lab houses a Thermo/Nicolet Nexus 6700 FTIR spectrometer and we used a Nicolet "Smart Collector" which acquires reflectance in a bi-directional geometry. The FT-Raman module uses a 1064 nm excitation laser and an InPhotote™ portable Raman was recently added and uses a 785nm excitation laser. We use an ASD field spectrometer for measurement from 0.4 to 2.5 µm and a high resolution Ocean Optics system for measurement from 300 to 1000 nm with stable light sources in bidirectional geometries.

Samples were measured in bulk, using narrow fiber optic sensors or directly in the small optical beam of the FTIR instrument. Samples including the endolithic or biologic layers were measured to contrast with uncolonizezd areas. In order to differentiate organic from inorganic absorption features samples were originally measured and then baked to 500C to destroy the organic material and then re-measured. Communities were examined under SEM and petrographic microscopes in order understand the relationship of the community to the grains of the host rock. X-ray diffraction was performed as a check on rock composition, but did not show any materials that were not identified through the spectroscopy. Measurement of isolated microbial cultures is planned as an independent check on the spectral features of mixed biology/rock samples.

Initial Results: Our first results include reflectance measurements from 0.4 to 25 µm. Technical difficulties have prohibited Raman measurements up to this point, but we anticipate these results in the near future.

Visible to 2.5 µm Characteristics: All the biological communities show clear chlorophyll features (Fig. 2). In particular, all of the endoliths have two features, one centered on 0.625 and 0.674 µm, characteristic of chlorophyll-a alone. Some samples also show weak features at 0.435 and 0.500 µm the former is also at-

tributable to chlorophyll-a and the latter may be a weak iron-oxide contamination in the rocks. Features between 2 and 2.5 µm are lacking in the endoliths. Denser hypolith and epilith communities have visible spectra more characteristic of common vegetation, showing a single broad feature and strong reflectance increase (the "red edge") indicating multiple chlorophyll pigments and these samples also have stronger features between 1 and 2.5 µm associated with C-H bonds. In the visible and short-wave infrared samples in gypsum show strong features from the rock, while those on sandstones have little interference from the rock matrix in the observed spectra.

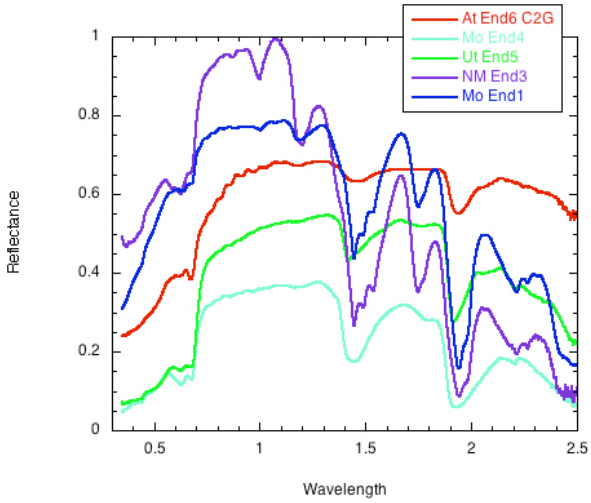

Figure 2: Reflectance spectra of endolithic communities from the Mojave (Mo), Utah (Ut), Atacama (At) and New Mexico (NM). NM End3 and Mo End1 are in gypsum, the others in quartz sandstones.

IR 2.5 to 7 µm: In the infrared range from 2 to 7 µm all samples have strong CH features from 3.33 to 3.54 µm (Figure 3). These often show the typical doublet with centers on 3.40 and 3.48 µm, although in some samples the separation is not well established. Features that are likely attributed to organics include: 4.49, 4.68, and 5.36 µm (seen in multiple samples) though specific band assignments have not yet been made. Unique narrow features are seen in the thicker lichen and hypotlith samples appear at 5.65, 5.75 µm. Broad features at 6.0, 6.44 µm are most likely due to water in either the structure of the biological community or included in the rock fabric. Some, non-gypsum host samples show a broad absorption feature between 4 and 5 µm that is probably due to small amounts of gypsum or other sulfate salts, though longer wavelength features associated with gypsum are not observed. Other features between 6 and 7.5 µm are not easily identified due to grain size and scattering effects that complicate the usual absorption and emission patterns.

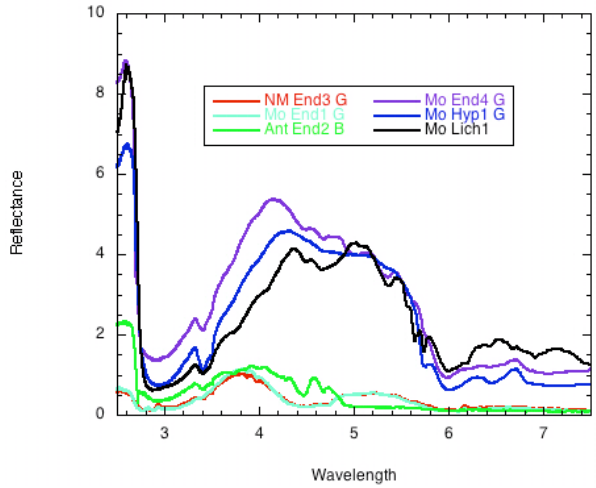

Figure 3: Mid-infrared reflectance spectra of selected biologic communities abbreviations as in Fig 2 with Antarctica (Ant).

TIR Range. 7 to 25 µm: Signatures at these wavelengths are dominated by the mineral components, quartz, sulfate and clay. The quartz-rich sandstones show interesting triplet features between 7 and 10 µm, but these are likely due to grain transparency and multiple crystallographic axes contributing to the spectral signature. Common features of quartz are observed from 12.2 to 13 µm. The gypsum endolithic samples show characteristic sulfate feature centered on 8.7 µm and near 15 µm. At wavelengths longer than 16 µm only mineral features are evident within the signal to noise of this method.

Summary: Spectroscopic methods are able to uniquely separate organic from non-organic constituents. The most promising spectral region is also the most difficult to interpret, the range from 4 to 7 µm, where features from aromatic and aliphatic CH bonds occur, but where scattering, absorption and grain size effects mix in a non-linear fashion. Strong and well-known features due to protein pigments and C-H are easily recognized with modest (mm) spatial resolution on these samples at other diagnostic wavelengths. Weak signatures remain problematic, particularly between 2 and 2.5 µm, supporting broad wavelength coverage in planetary exploration applications.

References: [1] Stuart et al. *Modern Infrared Spectroscopy*, Wiley, 1998. [2] Gaffey, et al. Ch. 3 in *Remote Geochemical Analysis*, Cambridge, 1993. [3] Dalton, et al. *Astrobiol.*, 3(3), p. 505, 2003. [4] Cruikshank, et al. *Icarus*, 193(2), doi:10.1016/j.icarus.2007.04.036. [5] Dong et al. *JGR*, 112, G02030, doi:10.1029/2006JG000385, 2007. [6] Sharma et al. *Spectrochim. Acta A*, 68(4), p. 1036, doi:10.1016/j.saa.2007.06.046, 2007.