BUILDING A BIOSIGNATURE IMAGING, SPECTRAL AND THIN SECTION LIBRARY TO SUPPORT UPCOMING MARS SURFACE MISSIONS.

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Introduction: Identifying minerals, organics, and potential biosignatures within individual rock and sediment samples is an important part of both terrestrial field and planetary surface exploration studies. To help with this effort, we are building a library of spectra, images, and thin sections of the associated minerals and biosignatures contained in potential analog rocks and sediment samples for Mars. We have been characterizing the samples in the lab using Raman spectroscopy at two different laser excitations, 532nm and 785nm, contextual and close up imaging with constrained lighting conditions, and hand sample and thin section analysis. Samples are generally characterized as is, without grinding to powders, to retain the critical spatial and geologic context and alteration history of of the rock sample.

Locating Biosignatures in Rock: An important component of sample analysis on future missions will be location selection on the sample. Prepared samples are mostly homogeneous, but natural rock samples are more heterogeneous and non-uniform. Analysis of the travertine sample shown in Figure 1 revealed β-carotene peaks in the more protected locations on the rock, while large flatter areas appeared devoid of spectral signatures pointing to life.In addition to minerals and rocks, biological compounds have unique Raman spectra of their own. ß-carotene, an organic compound whose presence indicates current or past life, has distinctive peaks at approximately 1000, 1153 and 1515 cm^{-1}, as seen in the microbial mat spectra shown below. Other biological substances, such as cyanobacteria, have their own spectra. An automated classifier could detect these biosignatures, paving the way for the discovery of present or past life elsewhere in our solar system.

As a proof-of- concept for the use of Raman spectroscopy to detect biosignatures in more naturally-occurring samples, spectra that potentially contained biosignatures were compared to the spectrum of the microbial mats, along with other known biological peaks. Here we present analysis from some of our samples, which Include travertine from Travertine Hot Springs, CA, and Atacama samples of gypsum, sinter, and halite as well some prepared laboratory samples containing various perchlorates.

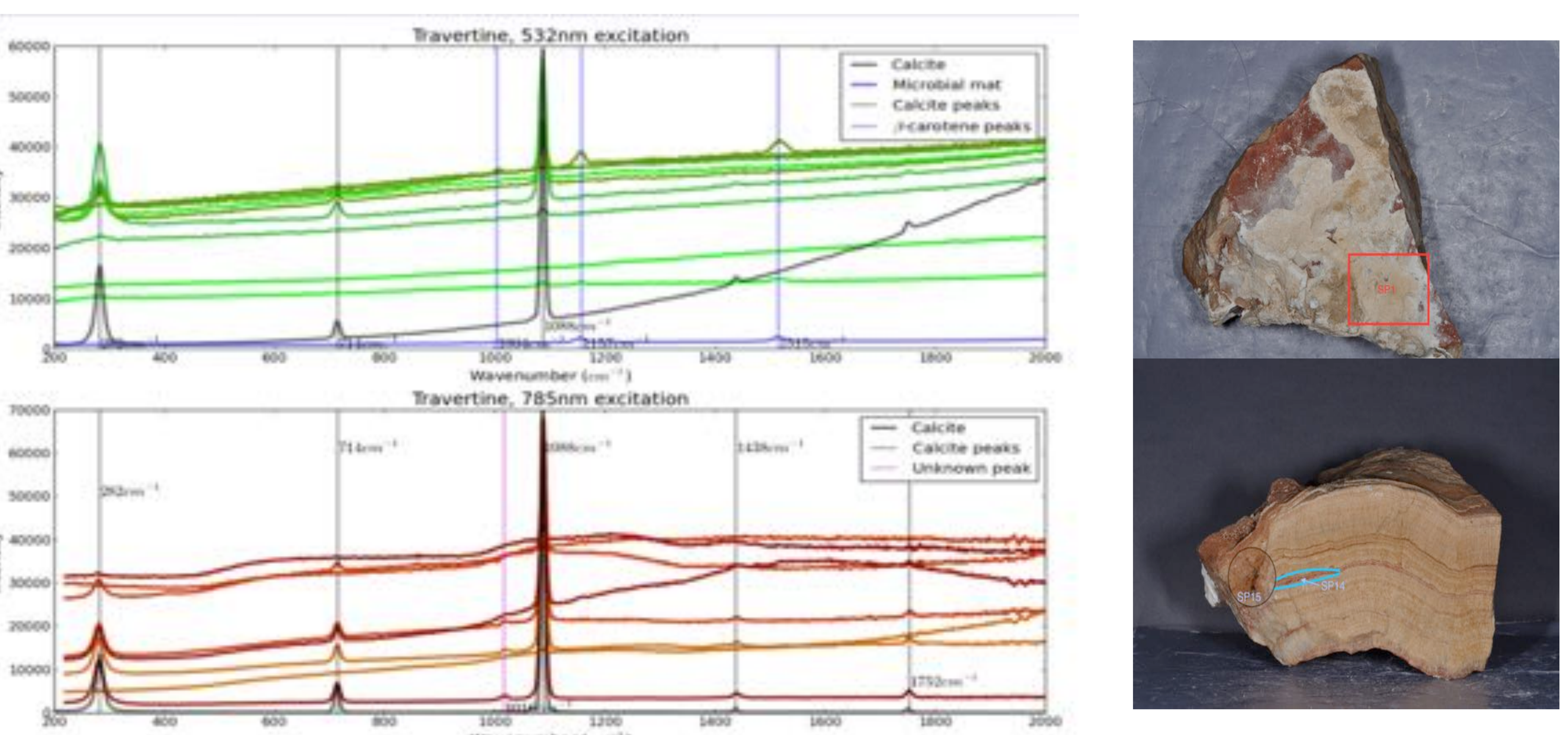

Figure 1: Travertine sample from Travertine Springs, CA. Image on left shows region where no biosignatures were identified. Image on right contained beta-carotene peaks in two protected regions circled. Plot shows several Raman spectra of the sample compared with β-carotene from a microbial mat (blue) and calcite (gray) spectra. Distinct calcite peaks as well as distinct peaks in the sample demonstrate the ability to detect both minerals and biosignatures in the same spectra.

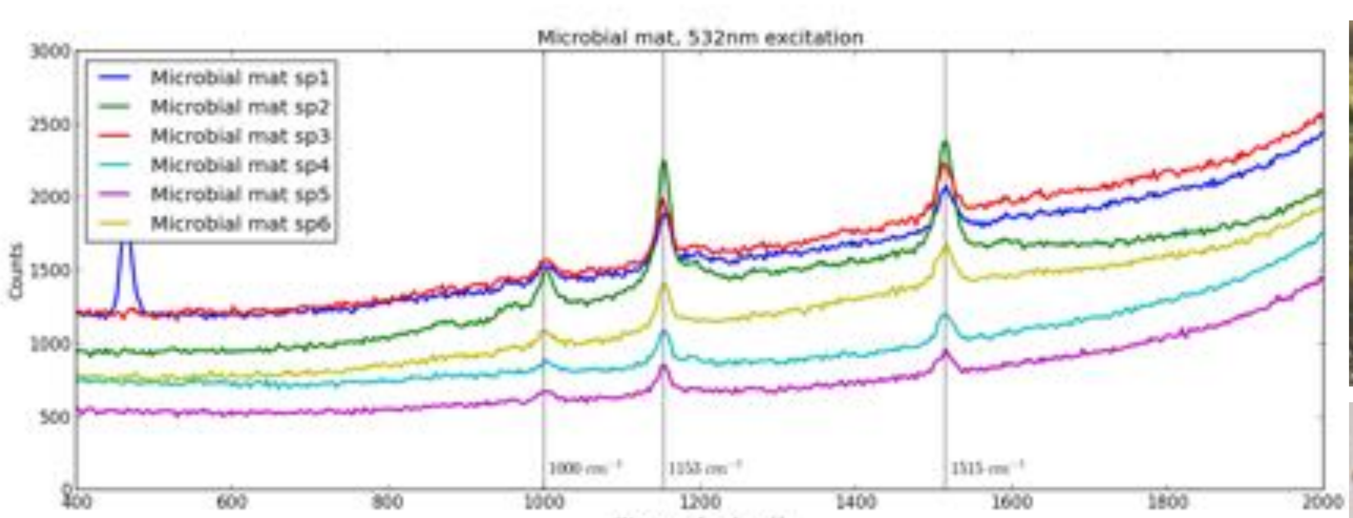

Figure 2: Raman spectra from microbial mats showing strong ß-carotene peaks. Spectrum 1 shows a prominent peak for the presence of quartz at ~464cm^{-1} which is the composition of the sand substrate. Images below show live and dried microbial mats. Microbial mats provided courtesy of Lee Bebout (ARC-SSX).

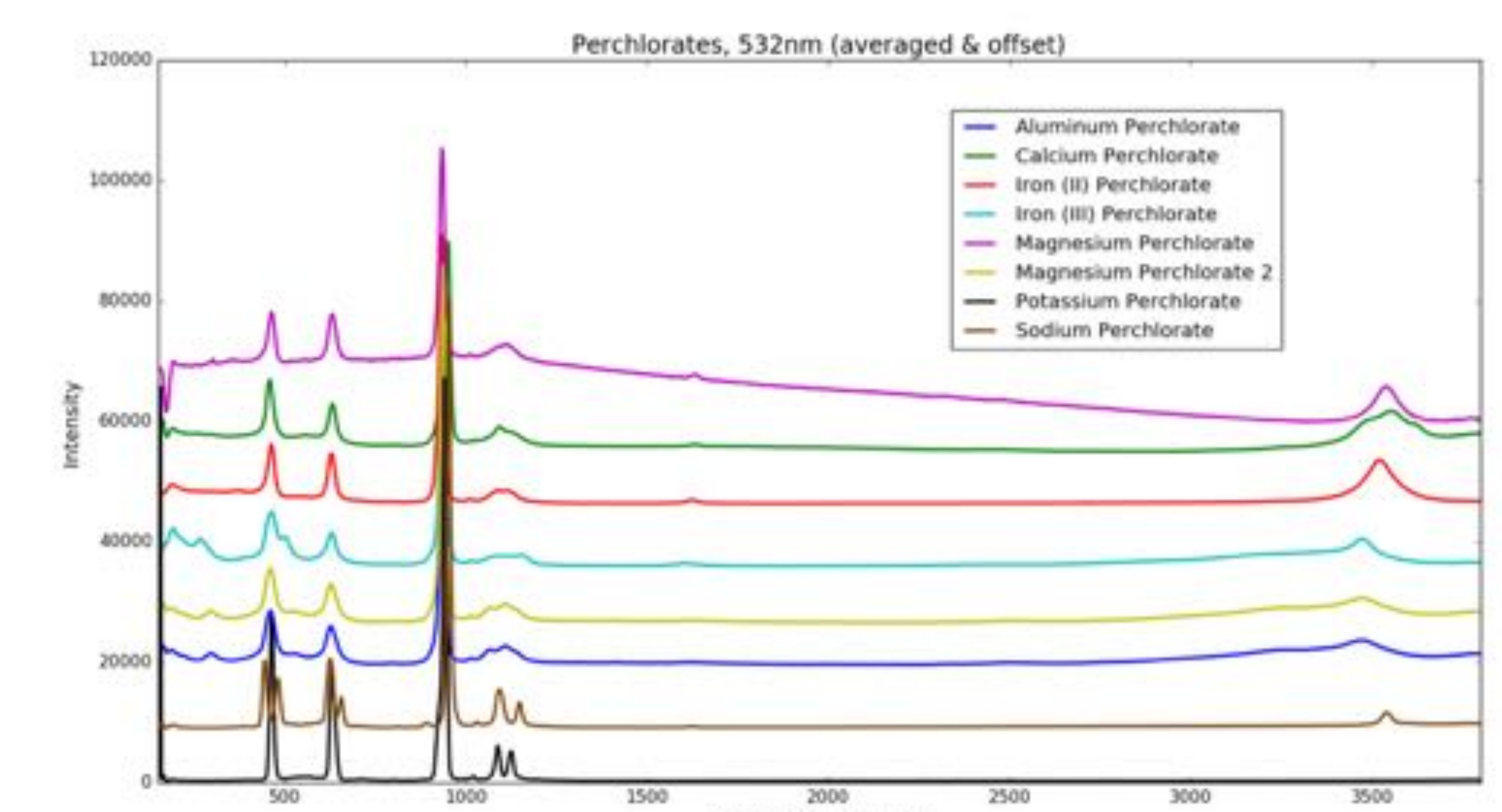

Figure 3: Raman spectra of various perchlorates. Perchlorates are thought to be common on Mars as well as in hyper-arid environments on Earth like in the Atacama. Peaks with wave numbers less than 1500 cm^{-1} are due to the perchlorate ion. Peak near 3500 cm^{-1} is due to the chemically bound water of hydration. Potassium perchlorate is the only perchlorate here that is not hygroscopic and therefore does not have a peak near 3500 cm^{-1}

Atacama Samples: The Atacama desert in Chile provides a terrestrial analogue for the surface of Mars. We have been using Raman spectroscopy on a number of rock samples from the Atacama desert to look for biosignatures. Below are some examples of samples from this unique region, which includes gypsum, sinter nodule, and a small salt rock, a larger gypsum sample, and a fine-grained sediment sample.

The smaller rock sample, determined by hand sample analysis to consist primarily of halite salts. Halite, on its own, lacks significant diagnostic Raman peaks, but contained noticeable biosignature peaks in multiple transects. A selection from one of these transects is shown in figure 5, along with a spectrum taken from a microbial mat that shows the three major β-carotene peaks. All three peaks are visible in the sample spectra, a clear indication of the presence of β-carotene.

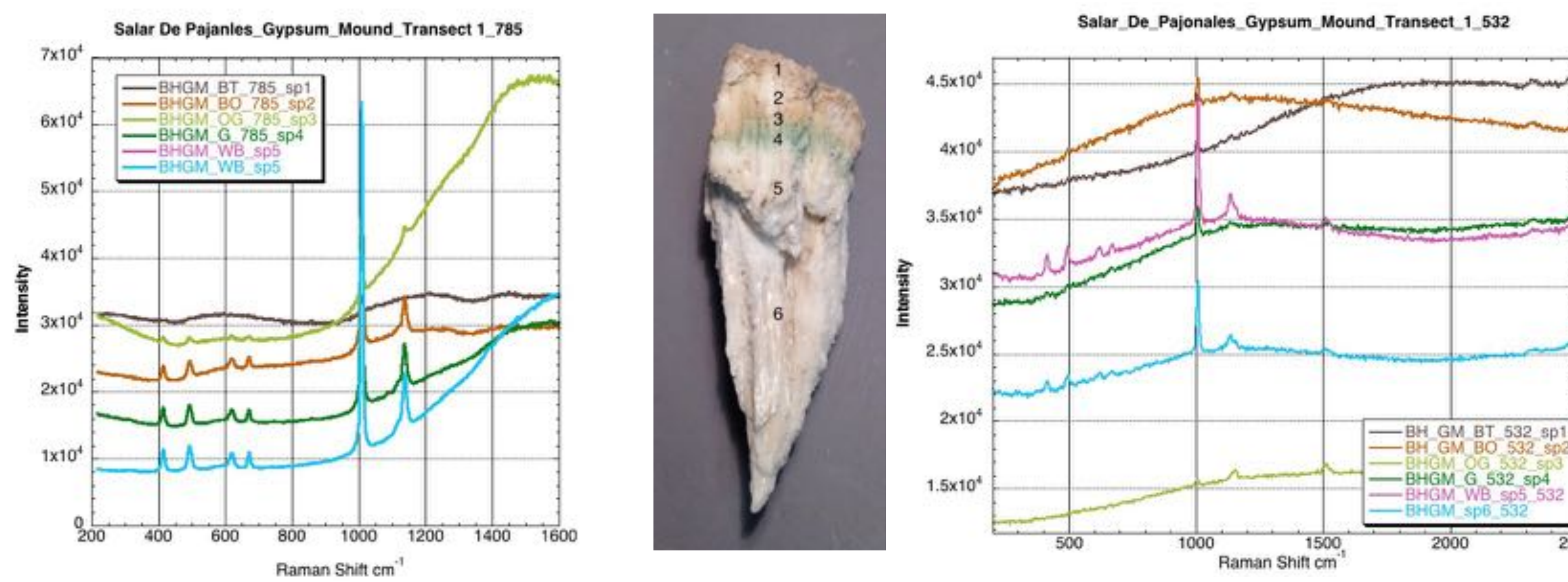

Figure 4: (above) Sample taken from Salar de Pajonales (SP) which is an evaporitic basin located in the Altiplano Puna (AP) at ~ 3,517 m in an arid climate (25° 10'S/68° 49) with annual rainfall <1 cm/yr. The AP includes broad, internally drained endoreic depocenters nestled among the Andean volcanoes. It comprises a large evaporitic area, which has evidence of former subaqueous gypsum beds precipitated during higher saline-lake levels at the Pleistocene/Holocene transition.

We have imaged and taken vertical transects (transect 1 shown here) of Raman spectra through sample using both our 532 nm and 785 nm laser excitations. In the 532 nm laser excitation, spectra 5 and 6 show prominent gypsum peaks as well as β-carotene peaks. Spectra 3 shows distinct β-carotene peaks while those in spectra 2 and 4 are more subtle. In the 732 nm laser excitation, spectra 2-6 show prominent gypsum peaks. Sample provided by Nancy Hinman, University of Montana.

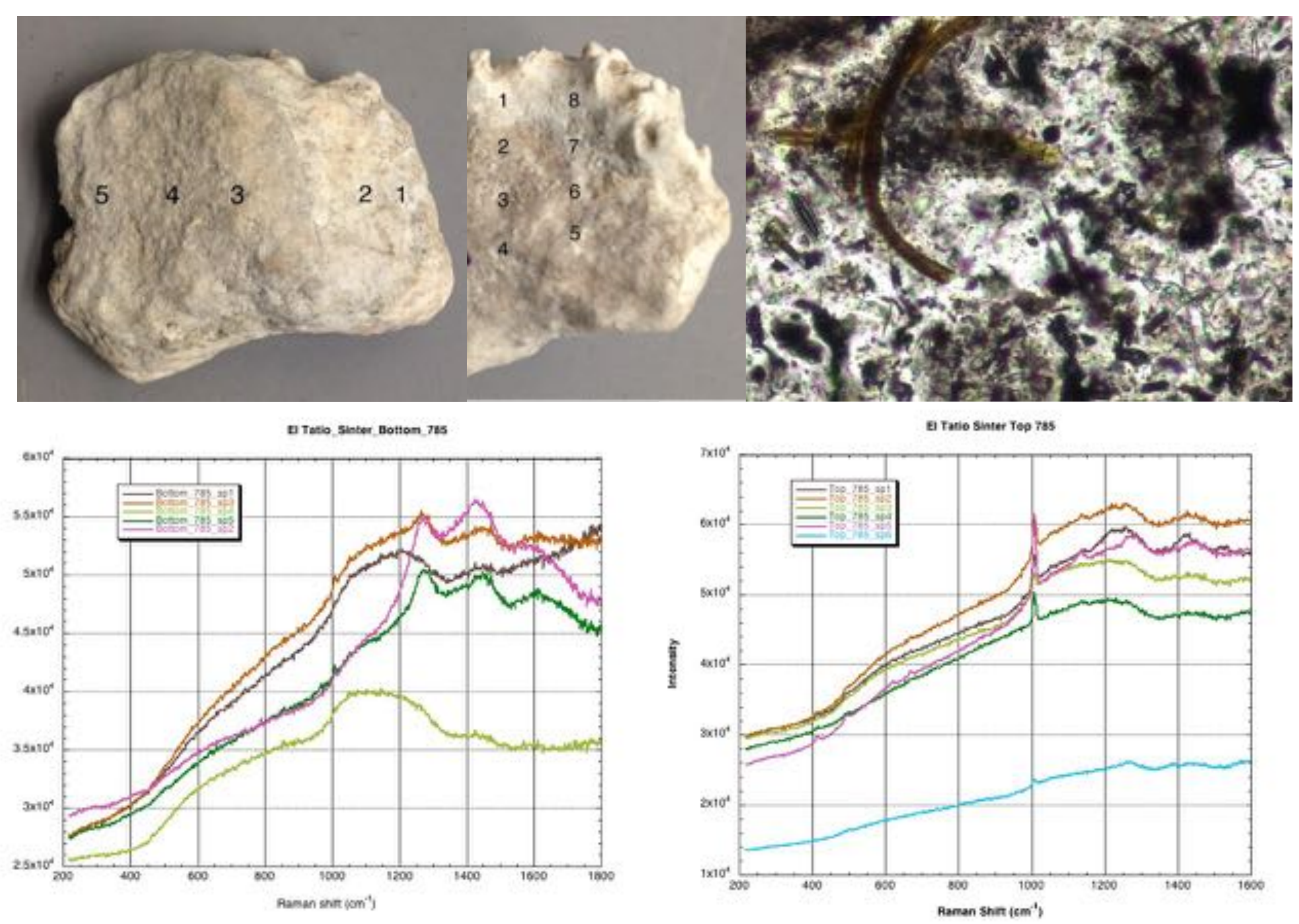

Figure 5: left El Tatio, located in the Atacama, is the third largest geothermal center on Earth. Hot springs and geysers form siliceous sinters that precipitate along with evaporative salts, iron oxides, and more exotic accessory phases.

Active opaline silica-depositing hydrothermal ecosystems preserve fossil information with high morphological and chemical fidelity.

Images show Raman spectral locations on the bottom (left most image) and on the top (middle image) of sinter sample . Right most image is a thin section which shows the classic overall texture of sinter with its amorphous or micro-crystalline structure. Thin sections show ~5% crystalline quartz, ~2% plagioclase feldspar, and ~ 5% hornblend. Microbial structures are visible throughout the thin section. Thin Section image taken at ~10x magnification.

Raman spectra taken at 785 nm laser excitation. Preliminary analysis shows gypsum, especially at top sp5, and organic compounds, possibly β-carotene. Overall fluorescence may indicate the presence of salts, halite in particular, and broad peaks > 1000 cm^{-1} suggest the presence of organic constituents.

Sample provided by Nancy Hinman, Univ. of Montana.

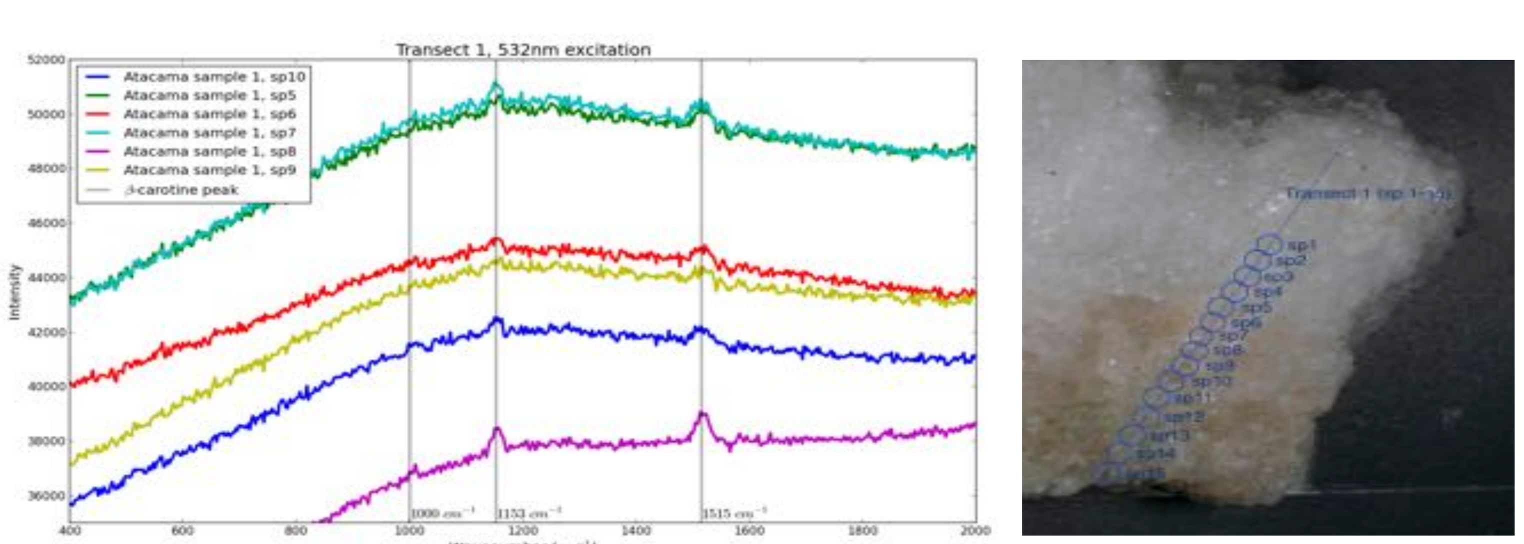

Figure 6: Spectra sp5-10 (left), sample (right) showing transect 1, from which spectra were taken. Although the overall rock spectra shows florescence and little in the way of prominent peaks, which can be suggestive of halite (which the hand sample analysis confirms), the spectra also contains some diagnostic peaks of β-carotene peaks (highlighted). Atacama salt sample provided by Alfonso Davila (NASA ARC/SSX).

Summary: The potential detection of biosignatures and organics in natural rock and sediment samples using Raman spectroscopy, especially in combination with imaging and other analysis, is promising. Versatility and ease of use make Raman an ideal candidate for use in future missions to Mars and beyond.

A goal of our research will be to provide an interactive, online library of samples containing Raman spectral transects, contextual and close-up images, and hand and thin section analysis for the community's use and to help support NASA 's Mars 2020 and other future surface missions. Ultimately, we are also interested in using this analyzed library to develop image and spectral analysis algorithms that can automatically classify the minerals and biosignatures contained in samples to support future planetary surface missions as well as remote terrestrial field studies. The addition of machine learning makes it possible for real-time onboard analysis, saving time on command cycles and returned data volume. for planetary missions. It would also be valuable for assisting in automated sample analysis while out in the field in terrestrial studies.

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