BIOSIGNATURE PRESERVATIONS IN GYPSUM VEINS AND MINERAL CRUST OF THE ATACAMA DESERT AS AN ANALOG FOR MARS. M. Weng[1], M. Millan[2], E. Zaikova[2], J. Bevilacqua[2] and S. S. Johnson[2], [1]Washington University in St. Louis (One Brookings Drive, St. Louis, MO 63130, margaret.weng@wustl.edu), [2]Georgetown University (3700 O Street NW, Washington, DC 20057).

Introduction: The first science goal for NASA's Mars exploration program is to determine if life ever arose on the planet [1]. One of its most challenging aspects is how to direct the investigation of the martian surface without being able to directly analyze martian samples in a laboratory. Earth environments as analog models for Mars are a good way to study how extreme conditions can support and preserve life, which may then inform targets of interest for rover exploration and other remote scientific investigations. In this study, we investigated the biosignature preservation capacity of two Mars-like environments in the Atacama Desert: halite crust from lowland dry lakebeds, and gypsum veins highly similar in appearance to those discovered by the Opportunity and Curiosity rovers.

Study Site: The Atacama Desert in Chile is a well-known Martian analog because of its extremely low precipitation, large daily temperature fluctuations, and high solar radiation [2]. NASA has used the Atacama Desert to test Mars rover instruments used to detect biosignatures, such as testing by the ARADS team conducted through NASA Ames [3]. Gypsum veins are an excellent visual match to those found on Mars, and appear to have formed by similar processes (see Figures 1 and 2). Halite crusts were also explored due to the fact that Mars contains evidence of many ancient lakes and lake deltas, including a potential landing site for the Mars 2020 rover at Jezero Crater. Therefore, studying the ability of lake crusts in a Mars-analog environment to preserve biosignatures could provide targets of interest for current rovers and future missions [4].

Methods: Samples were collected in triplicate using organically clean procedures (solvent-washed spatulas and glassware that were ashed overnight at 550ºC). Samples were cooled upon collection and then placed in a -80ºC freezer upon return to the laboratory.

Our investigation then utilized pyrolysis-GCMS to isolate and identify volatile compounds within these materials, as well as scanning electron microscopy (SEM) and energy-dispersive x-ray spectroscopy (EDS) for visualization of the materials' structures and mineralogy.

Pyrolysis-GCMS investigation was performed using a Frontier Pyrolyzer and Thermo-Fisher GC-ISQ. Two types of analysis were utilized on each sample—ramp pyrolysis and flash pyrolysis—and the results were compared to understand the variability of data (if any) between these methods. Ramp pyrolysis was performed on 10mg of sample using a 35ºC/min ramp temperature pyrolysis to 850ºC, and cryotrapping of the volatiles released after heating the solid analogs to mimic the method used on the Sample Analysis at Mars (SAM) instrument aboard NASA's Curiosity Rover [5]. We also executed flash pyrolysis of 10mg of sample at 850ºC for 1 minute with no cryotrapping. GCMS runs were performed on all samples directly after pyrolysis.

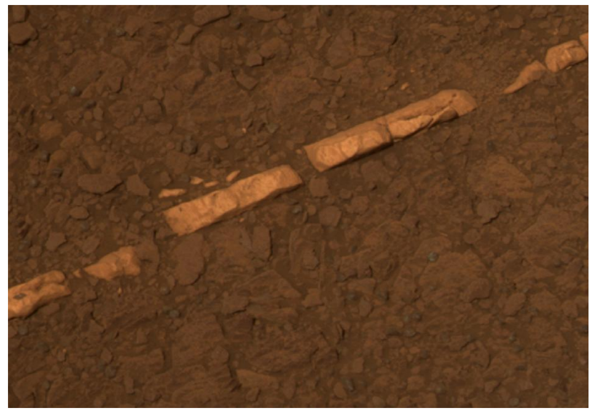

Figure 1: Gypsum vein "Homestake" found by Mars Rover Opportunity. Credit: NASA/JPL-Caltech/Cornell/ASU

Figure 2: Gypsum vein "VM3" sampled in the field.

For SEM and EDS, samples were fixed to metal viewing stubs using carbon tape and examined using a Zeiss SUPRA55-VP Scanning Electron Microscope at 1 kV. Samples were also examined at 20 kv using INCA EDS software on the same instrument for mineralogical confirmation and elemental spatial mapping.

Results: Several compounds were identified via pyrolysis-GCMS that were common to both halite crust bons/PAHs, sulfur compounds (S6 and S8), carbon dioxide, and amino acid building blocks or modified amino acids. The amino acid component R-(-)-2-amino-

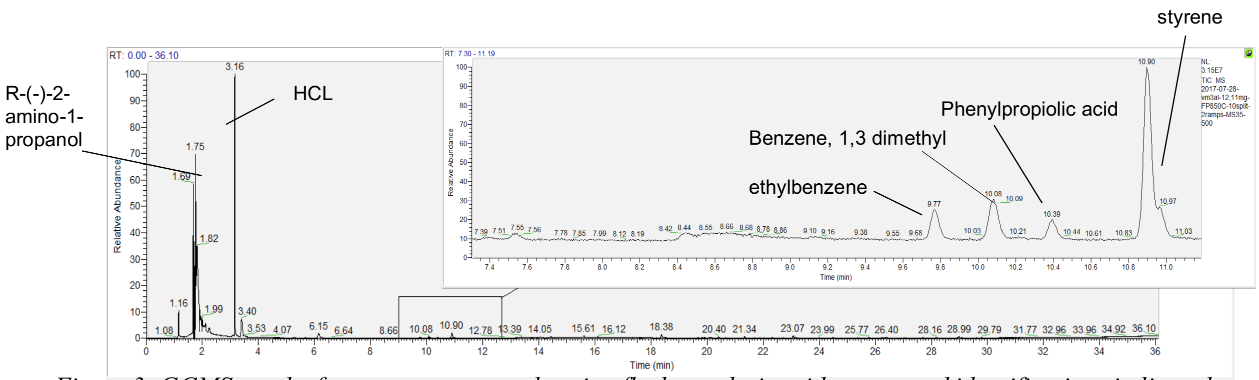

Figure 3: GCMS results from a gypsum sample using flash pyrolysis, with compound identifications indicated on peaks

1-propanol was identified in gypsum samples, whereas L-cysteine sulfinic acid, a modified amino acid, was identified in halite. Phenlypropiolic acid, a type of carboxylic acid, was also identified in gypsum veins.

SEM imaging and EDS confirmed structure and minerology of all samples. EDS detected the presence of sulfates within the halite crust, which was confirmed by the detection of sulfur compounds by pyrolysis-GCMS.

Discussion: The detection of amino acid building blocks or modified amino acids in both gypsum veins and halite crust indicates that both environments have the ability to preserve organic molecules and biosignatures. Detection of organic material in terrestrial sulfates such as gypsum has also been confirmed by Aubrey et al [6], who suggest that the longevity of preservation of amino acids in sulfate minerals makes them targets of interest in the search for life on Mars.

We plan to undertake further investigation using N-methyl-N-(tert-butyldimethylsilyl)-trifluoroacetamide (MTBSTFA), a derivitizing agent present in seven of the SAM instrument's sample cups in Mars. This will aid with pyro-GCMS detection of amino acids and potentially reveal even more preservation of organics. The detection of phenlypropiolic acid in gypsum veins is significant because carboxylic acids are specifically targeted as compounds of interest. Their detection on Mars could indicate the presence of evolved organics in martian oxidizing environmental conditions [7].

SAM-like results using ramp pyrolysis were different than flash pyrolysis runs, and returned fewer compounds. The difference between these two methods should be investigated further in order to determine how best to detect martian biosignatures.

Polycyclic aromatic hydrocarbons (PAHs) are common on Earth as well as on meteorites and comets. They can be produced by atmospheric and hydrothermal processes as well as through biological generation. PAHs have not yet been detected on Mars using SAM: however, chlorohydrocarbons have been identified on the martian surface. Some hypothesize that chlorohydrocarbons could be produced through reactions between perchlorates and Martian organic molecules, however, this result could also be an artifact of the SAM instrument. Adding perchlorates to these samples could help determine whether chlorohydrocarbons can form in situ via reactions with PAHs [8].

This ongoing work demonstrates the biosignature preservation potential of Mars analog sites in the Atacama Desert. Future experiments will allow us to better understand the most effective ways to detect organic molecules on the Red Planet, and which locations may be most fruitful for scientific investigation. To maximize the scientific return from Curiosity's exploration of Mount Sharp, and to prepare for future scientific missions, such as NASA's Mars 2020 rover and the European Space Agency's ExoMars rover, identifying sites which may store biosignatures and improving organic molecule detection techniques is more relevant than ever.

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