Biosignature Preservation Potential Among Diverse Calcium Sulfate Textures from the Atacama Desert, Chile.

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Introduction: Calcium sulfate minerals are widespread on both Earth and Mars and have the capacity to preserve evidence of life over geological timescales. Many distinct textural varieties of sulfate minerals occur and, depending on their depositional environment and diagenetic history, each may offer distinct pathways for biosignature preservation (i.e., "taphonomic windows"). However, these processes remain underexplored due to the high solubility of sulfates and, hence, their relative scarcity in the earliest rock record. Here, we explore the potential to preserve remnants of microbial life including carbonaceous microstructures resembling known organisms, as well as biomarkers preserved in the intracrystalline sulfate matrix.

Methods: We collected samples from the Oligocene-aged San Pedro Fm. and the Jurassic-aged Tonel Fm. from the Atacama Desert, Chile (Fig. 1). This environment is one of the driest deserts on the planet and serves as a unique Mars analog locality to study microbial taphonomy. Both sedimentary units were originally deposited in an evaporative lake environment, forming abundant evaporites including carbonates, gypsum, and halite. Here we focus on primary and secondary sulfates composed dominantly of gypsum and anhydrite. Notably, modern evaporative lakes adjacent to these deposits (e.g., Laguna Tebenquiche in the Salar de Atacama), are known to host abundant and diverse microbial organisms; We hypothesize that proximal ancient evaporative lake deposits preserve evidence of similar lake-dwelling organisms.

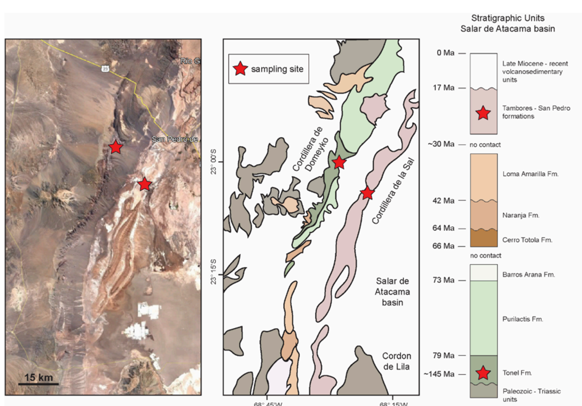

Figure 1: Geological context of sampled area. Sampling locations indicated by red stars.

Collected samples span a range of evaporite textures including water-column nucleated, bottom-nucleated, and displacive growth forms, as well as secondary textures including veins and anhydrite nodules. Representatives of each texture were thin sectioned and observed with a petrographic microscope. Elemental maps were generated using Energy-Dispersive X-ray Spectroscopy (EDS), and freshly exposed surfaces of hand samples were imaged with SEM at the Jet Propulsion Laboratory. The mineralogy and composition of thin sectioned samples was determined using Raman spectroscopy at Arizona State University. To investigate the preservation potential of biomarkers, we developed a modified Bligh-Dyer procedure to extract polar organics from the intracrystalline sulfate matrix. Organics were analyzed via Gas Chromatography Mass-Spectrometry at the Jet Propulsion Laboratory.

Results: Here we show that Jurassic-Cretaceous deposits from the Tonel Fm. and Oligocene deposits from the San Pedro Fm. preserve evidence of life in the form of fatty acid biomarkers and carbonaceous microfossil remains. Thin section observations reveal the presence of microstructures (filaments, spheres, and pilli) associated with carbonaceous material as identified by the presence of characteristic Raman "D" and "G" peaks (Fig. 2).

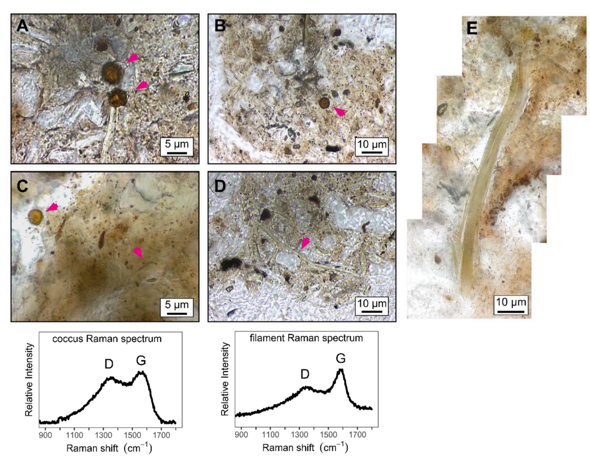

Figure 2: Carbonaceous microstructures identified in thin section. A-E: Samples retain spherical and filamentous structures whose size and morphology are consistent with known microorganisms. Their composition consists of carbonaceous micromaterial as indicated by characteristic Raman "D" and "G" bands (bottom panels).

Evaporative sulfates analyzed via bulk extraction methods were shown to retain fatty acids, detected as derivatized fatty acid methyl esters (FAMEs). 10 out of

12 analyzed samples retained fatty acid abundances significantly above the procedural sand blank background (e.g., Fig. 2). FAMEs generally exhibit an even-over-odd predominance, with highest abundances occurring as saturated C:16 (methyl palmitate) and C:18 (methyl stearate) varieties. Laminite textures were observed to retain the highest abundance and diversity of biomarkers compared to other textural varieties.

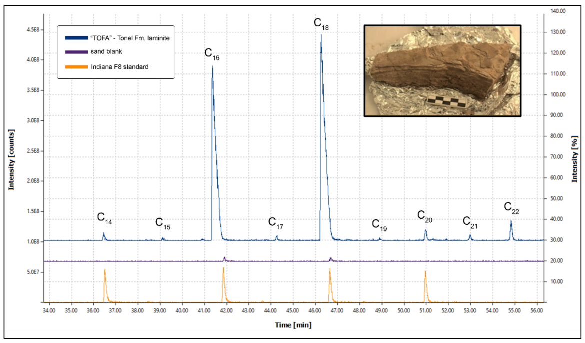

Figure 3. Representative chromatogram of organics extracted from Tonel Fm. laminite sample (blue). Purple chromatogram (middle) represents the procedural sand blank, and the orange chromatogram (bottom) represents a fatty acid standard obtained by Schimmelmann Research.

Discussion: Preliminary results indicate that ancient sulfates from these units likely preserve direct evidence of microbial life. In combination, the morphology, carbonaceous composition, and occurrence in previously habitable (and likely inhabited) environment suggest that sulfate-entombed microstructures (e.g., in Fig. 2) represent cellular microfossils derived from the original evaporative lake environment. The presence of organic biomarkers further reinforces this hypothesis. The detection of labile FAMEs suggests that such environments are capable of exceptional preservation over geologic timescales. These observations are consistent with other studies that have found exceptional preservation occurring under extremely arid conditions (a concept termed "xeropreservation" by Wilhelm et al., 2018 [1]).

The combined approach of bulk organic geochemistry and spatially resolved analyses lends favorably towards understanding the "what and where" of such samples, i.e. "what" specific molecular biosignatures exist and "where" texturally might they occur. This combined approach suggests that different evaporative sulfate textures may have different affinities for organic preservation; In particular, we found that the highest diversity and abundance of organic biomarkers were present among laminite textures. In terms of microfossil preservation, we find that the highest abundance of such structures was typically found among displacive-growth sulfates exhibiting solid clay-bearing inclusions within their crystalline matrix. These observations suggest that clays play an important role in the preservation of such materials, likely due in part to the organic sorption capacities of interstitial clay layers. We posit that total encapsulation of clay + biosignature assemblages by sulfates may represent a unique taphonomic window for exceptional preservation over geologic timescales.

We suggest that sulfates on Mars may also exhibit texture-dependent discrepancies in their organic preservation potential. Our results highlight the importance of characterizing sulfates with respect to known evaporative facies frameworks (e.g., [2]) where possible. In particular, our results suggest that displacive-growth sulfates, formed within saturated benthic muds, and laminites formed by cyclical hydrological processes (e.g., regular freshening) may have the best potential for preserving signs of past life.

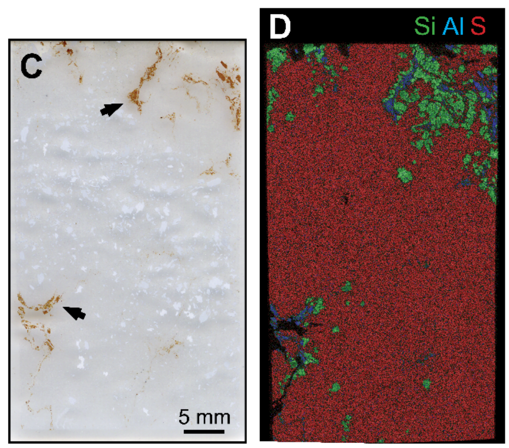

Figure 4. EDS maps of sulfate thin sections show solid inclusions of clay-bearing material (as indicated by their Si-Al composition). Such areas were observed to have higher occurrences of carbonaceous microfossil structures. The incorporation of solid inclusions in displacive growth style sulfates likely represents an important taphonomic window to preserve evidence of microbial life in sulfate-precipitating environments.

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References:

[1] Wilhelm, M.B., et al. (2017) *Organic geochemistry*, *103*. [2] Warren, J.K. (2006) Springer Sci. & Business Media.