

ORGANICS DETECTION FROM THE EL TATIO GEYSER FIELD DIGITATE STROMATOLITES, WITH IMPLICATIONS FOR ORGANICS DETECTION IN COMPARABLE DIGITATE STRUCTURES FROM COLUMBIA HILLS IN GUSEV CRATER, MARS. A. J. Williams¹, F. Juarez Duran², D. Hu³, P. Thompson⁴, C. Muñoz-Saez⁵, ¹Department of Geological Sciences, University of Florida, 241 Williamson Hall, Gainesville, FL, 32611, amywilliams1@ufl.edu, ²Colorado College, ³Brown University, ⁴Duke University, ⁵University of Nevada, Reno

Introduction: Volcanism and water on Mars produced habitable regions where geothermal energy interacted with the hydrosphere, presenting an ideal environment to support life on Mars, if it arose. The Columbia Hills region in Gusev crater has evidence for volcanic hydrothermal environments with outcrops of opaline silica forming nodular and digitate silica structures [1]. Similar morphologic features with comparable mineralogy have been identified in the nodular and digitate stromatolite-like structures within active hot spring and geyser discharge channels from the **El Tatio geyser field** in the Chilean Atacama desert [1]. El Tatio is an ideal Mars analog due to its aridity, strong winds, daily temperature changes, high elevation and UV radiation. These stromatolites include complex sedimentary structures generated by both abiotic and biotic processes, and provide a compelling terrestrial analog for the comparable features at Columbia Hills. At El Tatio, these sinters provide potential locations to concentrate and preserve organic matter as biosignatures. This work explores the organic load in El Tatio stromatolites and the potential for organics detection in similar Martian features with the SAM instrument on NASA's *Curiosity* rover.

Methods: El Tatio geyser samples were collected using organically clean methods (solvent washed and ashed (500°C for 8 hours) tools and glass jars) from 3 geyser discharge channels. Samples were frozen for transport to the lab. In the lab, samples were broken open with an ashed chisel and broken fragments were ground to a powder in an ashed mortar and pestle. Ground samples destined for Bligh & Dyer extraction were extracted with a mix of H₂O, MeOH, DCM at a 4:10:5 ratio, and vortexed, sonicated, and shaken before the solvent mix was decanted. This was repeated 3x and the DCM from the 3 extractions was separated, pooled, and dried down under sterile N₂ to 2mL. Samples were derivatized using medium acid methanolysis.

GC-MS: Samples were analyzed on an Agilent GC-MS coupled to a Frontier pyrolyzer. Samples analyzed for acyclic hydrocarbons were pyrolyzed at 600°C for 0.2 min. The oven program ramped from 50°C to 300°C at 20°C/min with a 10 minute hold. Samples analyzed for fatty acids were subject to TMAH thermochemolysis at a ratio of 1μL TMAH to 1mg sample, with the same pyrolyzer and oven programs as for acyclic hydrocarbons. TMAH is used to liberate and methylate fatty acids bound in phospholipids as well as free fatty acids. Samples analyzed with ramp pyrolysis were pyrolyzed from

50 to 600°C at 35°C/min (comparable to the SAM instrument oven ramp rate).

One μL of the solvent extracted sample was directly injected onto the GC-MS front inlet. The inlet was held at 280°C. The oven program ramped from 70°C to 130°C at 10°C/min, then ramped at 4°C/min to 310°C with a 5 minute hold. Molecules were identified using ChemStation software and comparison with known retention times.

Results & Discussion: Alkanes from C₇ to C₃₀ were detected with a weak odd-over-even chain length preference in alkane distribution <C₂₃. C₁₅ and C₁₇ are the dominant alkanes in the lipid profile. The ramp pyrolysis technique yielded ca. 10x the alkanes as the samples analyzed with the flash pyrolysis method (Fig. 1). Alkanes >C₁₈ were mostly lacking in ramped pyrolysis.

FAMES from C₈ to C₂₈ were detected including monounsaturated FA (MUFA) and methyl-branched FA. C₁₆ and C₁₈ are the dominant FAMES due to the abundance of these lengths in both bacterial and eukaryotic cellular membranes. FAMES >C₁₈ are likely wax esters derived from higher plants [2]. The even-over-odd chain length preference in FAME distribution is characteristic of a modern microbial community within the stromatolitic layers. The flash pyrolysis technique yielded >30x the FAMES as the samples analyzed with the ramp pyrolysis method. Although methyl-branched FA were detected with flash pyrolysis, MUFAs were not identified (Fig. 2).

These results indicate that ramped pyrolysis is optimal for acyclic hydrocarbons, and flash pyrolysis (under 600°C to accommodate TMAH thermochemolysis) is optimal for FAMES. These results are consistent with previous studies [3].

Modified Bligh & Dyer extraction yielded FAMES and alkanes from C₁₄ to C₂₆ and C₁₇ to C₂₉, respectively, and included a variety of methyl-branched FA (Fig. 3A). Fewer shorter chain FAMES and acyclic hydrocarbons were detected with solvent extraction relative to py-GC-MS. However, pyrolysis yielded far more by-products and created more complex chromatograms that can be difficult to interpret. In general, pyrolysis yields a comparable to superior abundance and diversity of FAs and acyclic hydrocarbons in silica sinter mineralogies with a modern microbial community as compared with traditional Bligh & Dyer extraction, which is far more time and resource intensive. However, the greater number of pyrolysis byproducts can make chromatogram interpretation more difficult.

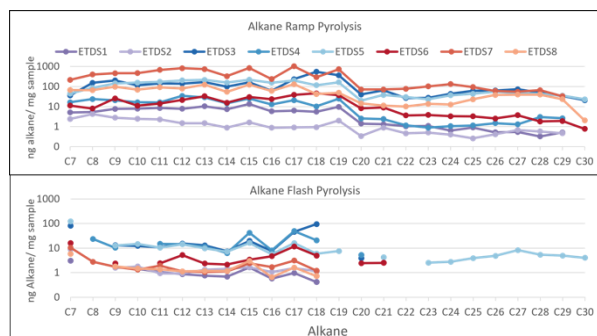


Figure 1. Alkanes detected with and 35°C/min ramp pyrolysis and 600°C flash pyrolysis.

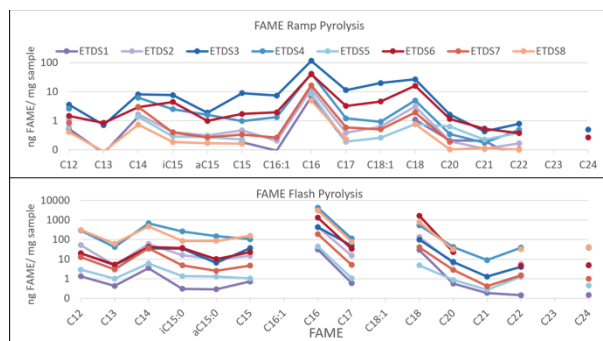


Figure 2. FAMES detected with 35°C/min ramp pyrolysis and 600°C flash pyrolysis.

These results suggest that these suites of organics, if present and recently formed, should be detectable in Martian hot spring samples with current py-GC-MS techniques. Other organics have been detected on Mars with SAM. Chlorinated hydrocarbons such as chlorobenzene and C₂ to C₄ dichloroalkanes were detected in the Sheepbed mudstone, Gale crater [5], and thiophenic, aromatic, and aliphatic organic compounds were found in the 3.5 Gy Murray Formation lacustrine mudstones, Gale crater [6]. Three medium-chain alkanes [7] and medium to high molecular masses, including derivatized molecules, have also been detected in samples exposed to SAM's MTBSTFA wet chemistry experiment [8]. SAM's other wet chemistry experiment, TMAH thermochemolysis [3], has recently been performed and yielded a variety of aromatic molecules including benzothiophene and methyl-naphthalene [9]. Results from these El Tatio experiments indicate that fatty acids, if present and preserved, are likely detectable with the SAM TMAH thermochemolysis experiment, and results may improve with the faster pyrolysis ramp of the MOMA [4] TMAH experiment onboard ESA's *Exo-Mars* mission.

Interpretation of these results are limited by the modernity of the El Tatio samples. El Tatio likely represents a snapshot of the Columbia Hills site in its active formation phase. Potentially billions of years of senescence and irradiation may have destroyed any residual organics within these Martian hot spring deposits [10, 11]. Future analog work should assess organics preservation in relict hot springs that approximate the Columbia Hills environment.

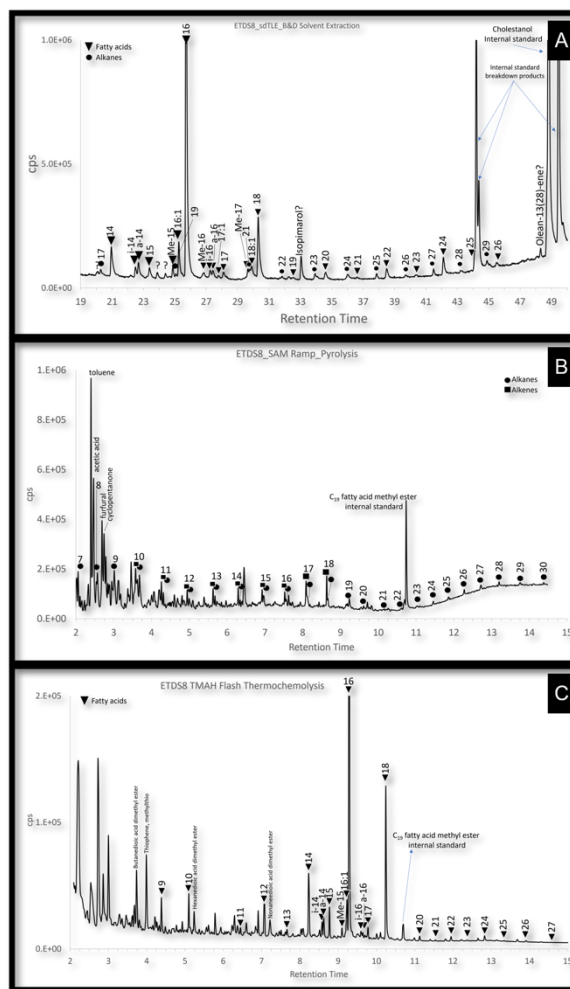


Figure 3. Comparison of solvent extraction (A) with neat pyrolysis (B) and TMAH thermochemolysis (C) techniques.

Conclusions: Acyclic hydrocarbons and fatty acids were preserved in El Tatio stromatolite samples and detectable with benchtop versions of techniques available on the *Curiosity* rover. Space flight-like pyrolysis was comparable in performance to time-intensive solvent extraction techniques. These results demonstrate the importance of sending GC-MS instruments to Mars to support continued exploration for biosignatures, especially in Martian hydrothermal systems.

References: [1] Ruff, S.W. and Farmer, J.D. (2016) *Nature Comm.*, 7, 13554. [2] Eglinton, G., and Hamilton, R. J. (1967) *Science*, 156, 1322-1335. [3] Williams, A.J. et al. (2019) *Astroble.*, 19, 522-546. [4] Goesmann, F. et al. (2017) *Astroble.*, 19, 522-546. [5] Freissinet, C. et al. (2015) *J. Geophys. Res.* 120, 495-514. [6] Eigenbrode, J.L. et al. (2018) *Science*, 360, 1096-1101. [7] Freissinet, C. et al. (2019) *Mars 9 Conf.*, 6123. [8] Millan, M. et al. (2021) *Nat. Astron.*, 2397-3366. [9] Williams, A.J. et al. (2021) *LPSC 52*, 1763. [10] Tan, J. and Sephton, M.A. (2019) *Astroble.*, 53-72. [11] Teece, B.L. et al. (2019). *Astroble.*, 537-551.