ORGANICS PRESERVATION AND 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. Williams[1], C. Muñoz[2], S. Shaner[1], D. Hu[3], P. Thompson[4], [1]Department of Geological Sciences, University of Florida, 241 Williamson Hall, Gainesville, FL, 32611, amywilliams1@ufl.edu, [2]Universidad de Chile, [3]Worcester Academy, Worcester, MA; [4]Ponte Vedra High School, Ponte Vedra, FL

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 stromatolites within active hot spring and geyser discharge channels from the **El Tatio geyser field** in the Chilean Atacama desert [1]. 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 and MOMA GC-MS instruments on the NASA *Curiosity* and ESA *ExoMars* rovers, respectively.

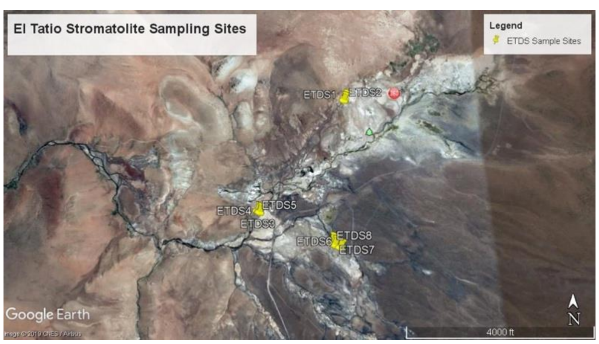

Figure 1. El Tatio geyser discharge sampling sites.

Table 1. Stromatolite sample details.

Site	Sample	Temperature	Distance from vent
1	ETDS2	24°C	2 m
	ETDS1	18 to 23°C	10 m
2	ETDS3	25 to 45°C	2 m
	ETDS4	20 to 28°C	4 m
	ETDS5	20 to 25°C	15 m
3	ETDS6	40 to 46°C	40 m
	ETDS7	20 to 23°C	65 m
	ETDS8	16°C	100 m

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 (Fig. 1; Table 1). Samples were frozen for transport to the lab. In the lab, samples were broken open (Fig. 2) with an ashed chisel and broken fragments were ground to a powder in an ashed mortar and pestle.

Figure 2. Cross section of El Tatio stromatolite.

GC-MS: Samples were analyzed on an Agilent GC-MS coupled to a Frontier pyrolyzer. Samples analyzed for alkanes were pyrolyzed at 600°C for 0.2 min (comparable to the MOMA instrument pyrolysis oven ramp of 200°C/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 alkanes. 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). Molecules were identified using ChemStation software.

Results & Discussion: Alkanes from C_7 to C_{30} were detected in the El Tatio samples with a weak odd-over-even chain length preference in alkane distribution $<C_{23}$. C_{15} and C_{17} are the dominant alkanes in the lipid profile. Alkanes $>C_{18}$ are consistent with wax from higher plants or algae [2]. The ramp pyrolysis technique yielded ca. 10x the alkanes as the samples analyzed with the flash pyrolysis method (Fig. 3).

FAMEs from C_8 to C_{28} were detected in the El Tatio samples, including monounsaturated FA and iso- and antiso-FA. C_{16} and C_{18} are the dominant FAMEs due to the abundance of these lengths in both bacterial and eukaryotic cellular membranes. FAMEs longer than C_{18} are likely wax esters derived from higher plants. 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.

A greater diversity of FAMEs, particularly in the wax ester lengths, was present with the flash pyrolysis method (Fig. 4).

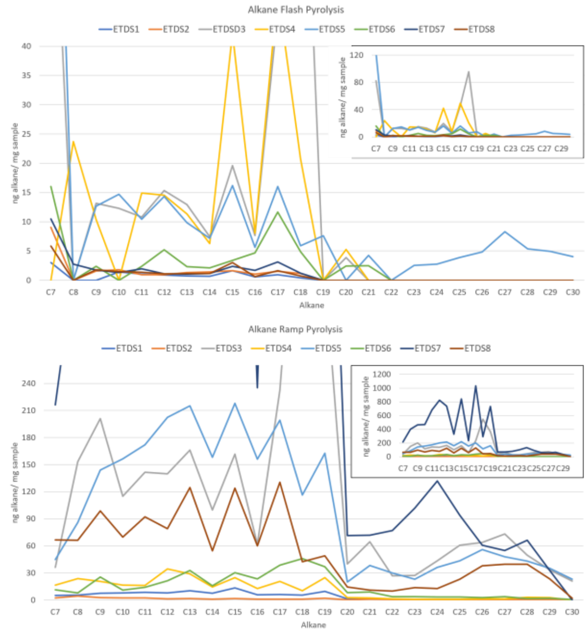

Figure 3. Alkanes detected with 600°C flash and 35°C/min ramp pyrolysis.

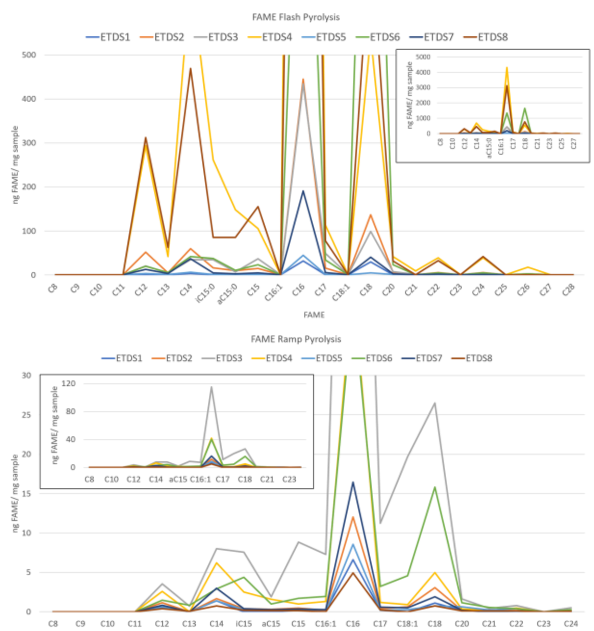

Figure 4. FAMEs detected with 600°C flash and 35°C/min ramp pyrolysis.

This study determined that organic alkane and fatty acid biosignatures are 1) preserved in the El Tatio nodular and digitate stromatolites and 2) detectable with a benchtop version of the pyrolysis and TMAH wet chemistry experiments on the NASA *Curiosity* rover SAM instrument [3] and the ESA *ExoMars* MOMA instrument [4].

The SAM-like 35°C/min pyrolysis ramp yielded superior results for the alkane fraction in both abundance of alkanes and diversity. The 600°C flash pyrolysis method yielded superior results for the fatty acid fraction in both abundance and diversity of fatty acids. Only the 35°C/min pyrolysis ramp is available on the *Curiosity* SAM instrument. These results suggest that alkanes, if present and recently formed, should be readily detectable in Martian hot spring samples with current GC-MS techniques. Other organics have been detected on Mars with SAM. Chlorinated hydrocarbons such as chlorobenzene and C_2 to C_4 dichloroalkanes were detected in the Sheepbed mudstone in Yellowknife Bay, Gale crater [5], and thiophenic, aromatic, and aliphatic organic compounds were found in the 3.5 Gy Murray Formation lacustrine mudstones of Pahrump Hills, Gale crater [6]. In more recent SAM experiments, preliminary analyses suggest the presence of select medium-chain alkanes [7] and medium to high molecular masses, including derivatized molecules [8], in samples exposed to SAM's other wet chemistry experiment, derivatization with MTBSTFA [9, 10]. SAM's other wet chemistry experiment, TMAH thermochemolysis [3], is capable of producing fatty acid methyl esters and has yet to be performed on Mars as of the time of this writing. Results from the El Tatio experiments indicate that fatty acids, if present, are likely preserved and detectable with the SAM TMAH thermochemolysis experiment, and results may improve with the faster pyrolysis ramp of the MOMA TMAH experiment.

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 during its formation. Potentially billions of years of senescence and irradiation may have destroyed any residual organics within these Martian hot spring deposits [e.g. 11, 12]. Future analog work should assess organics preservation in relict hot springs that approximate the Columbia Hills environment.

Conclusions: Alkanes and fatty acids were preserved in El Tatio stromatolite samples and detectable with benchtop versions of techniques available on the *Curiosity* and *ExoMars* rovers. These results demonstrate the importance of sending GC-MS instruments to Mars to support continued exploration for organic biosignatures, especially in Martian hot spring 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) *Astrobio., 19*, 522-546. [4] Goesmann, F. et al. (2017) *Astrobio.*, 655–685. [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. (2019) *Mars 9 Conf.*, 6210. [9] Buch, A. et al. (2006). *Planet. Space Sci.* 54, 1592–1599. [10] Mahaffy, P.R. et al. (2012). *Space Sci. Rev.* 1–78. [11] Tan, J. and Sephton, M.A. (2019) *Astrobio., accepted*. [12] Teece, B.L. et al. (2019). *Astrobio., in review*.