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PREPARATION FOR THE SAM TMAH WET CHEMISTRY EXPERIMENT ONBOARD CURIOSITY: ORGANICS DETECTION IN MARS-ANALOG ROCKS AND CANDIDATE LOCATIONS FOR THE *IN SITU* EXPERIMENT ON MARS. A.J. Williams^{1,2}, J.L. Eigenbrode², S.S. Johnson³, K.L. Craft⁴, M.B. Wilhelm⁵, S.S. O'Reilly⁶, J.M.T. Lewis², R. Williams², A. McAdam², C.A. Knudson², M. Millan^{2,3}, A. Buch⁷, C. Freissinet⁷, D. Glavin², R.E. Summons⁶, K.C. Benison⁸, C. Szopa⁷, R. Navarro-González⁹, V. Fox¹⁰, C. Malespin², P. Mahaffy², ¹University of Florida (amywilliams1@ufl.edu), ²NASA Goddard Space Flight Center, ³Georgetown University, ⁴Johns Hopkins University Applied Physics Lab, ⁵NASA Ames Research Center, ⁶Massachusetts Institute of Technology, ⁷CNRS - LATMOS, ⁸West Virginia University, ⁹Universidad Nacional Autónoma de México, ¹⁰CalTech

		C ₈	C ₁₀	C ₁₁	C ₁₂	C ₁₃	C ₁₄	C ₁₅	C ₁₆	C _{16:1}	C ₁₇	C ₁₈	C _{18:1}	C _{18:2}	C ₂₀	%TOC
Iron Oxides (+ clays)	Modern acidic	--	x	--	x	--	--	x	x	--	--	--	--	--	--	0.97%
		--	x	x	x	--	x	--	x	x	--	x	x	--	--	
	Older acidic	x	x	--	--	--	--	--	--	--	--	--	--	--	--	0.05%
	Sub-Eocene acidic	x	x	--	x	--	--	--	--	--	--	--	--	--	--	0.81%
	Eocene neutral	x	x	x	x	x	x	x	x	--	--	x	--	--	--	0.07%
	x	x	x	x	x	x	x	x	--	x	x	--	--	x		
Siliceous Sinter	Active Vent	x	x	--	x	x	x	x	x	x	x	x	x	x	x	0.24%
	Inactive Vent	x	x	--	x	--	x	--	--	--	--	x	--	--	--	0.02%
	x	x	x	x	x	x	x	x	--	x	x	x	x	--	--	
Carbonate Salts		--	--	--	--	--	x	x	x	x	x	x	x	x	x	nd
Carbonate/Sulfate Salts		--	--	--	--	--	x	x	x	--	x	x	--	--	x	nd
Carbonate Ooid		x	--	--	x	--	x	--	x	--	--	--	--	--	--	2.10%
	x	x	--	x	x	x	x	x	x	x	x	x	--	--	x	
Shale		x	x	x	x	x	x	x	x	--	x	x	--	--	x	32.57%
		x	x	x	x	x	x	x	x	x	x	x	x	x	x	

Table 1. FAME detection in Mars-analogous samples with variable mineralogies. 'X' = FAME detected, '--' = FAME absent. 'SAM-like 35°C/min pyro ramp analyses' = dark gray cells. '500°C flash pyrolysis analyses' = light gray cells. TOC = total organic carbon determined via loss-on-ignition ± 0.06%.

Introduction: The Mars Curiosity rover is ascending Mt. Sharp, in Gale Crater, exploring stratigraphic packages of rocks for evidence of habitability [1] and searching for organic compounds using the Sample Analysis at Mars (SAM) instrument suite. SAM includes a gas chromatograph mass spectrometer (GCMS) and sample pyrolysis ovens. SAM also has the capability of performing wet chemistry experiments, either by N-methyl-N-terbutyldimethylsilyltrifluoroacetamide (MTBSTFA) derivatization or tetramethylammonium hydroxide (TMAH) thermally assisted hydrolysis/methylation (THM). Coupled with wet chemistry experiments, the GCMS is capable of detecting large carboxylic acids and other hydrocarbons (e.g. lipid biosignatures). If present, these molecules may be bound into large macromolecules (e.g. biomolecules or kerogen) as they are often on Earth. On Mars, SAM will use the TMAH experiment onboard MSL to hydrolyze molecules, releasing them from their host macromolecules, and then methylate those molecules so they are sufficiently volatile for detection by SAM's GCMS [2]. Two of the nine wet chemistry cups on SAM contain the TMAH reagent; the other seven contain MTBSTFA [2]. Each TMAH cup contains an outer reservoir filled with ~ 500 µl of a 25% solution of TMAH in methanol (1:3v) with 25 nmol pyrene and 34 nmol 1-

fluoronaphthalene in solution. Inside is a second reservoir filled with ~12 nmol nonanoic acid that serves as the internal calibration standard. This project determines the effectiveness of the TMAH experiment to liberate organics from a variety of Mars-analogous rock samples.

Background: Rock samples were collected from a variety of Mars analogue environments. Samples include: *iron oxides* from a modern mineral precipitate and older surface gossan at Iron Mountain, CA; *mixed clays & iron oxides* in Sub-Eocene acid salt lake sediments and Eocene circumneutral lake sediments from Western Australia; *siliceous sinter* deposits from Icelandic hot springs at near-vent locations of active and recently inactive systems; *modern carbonate and sulfate salts* in lava tubes from Craters of the Moon National Monument, ID; *modern carbonate ooids* from Pigeon Cay, The Bahamas; and *organic-rich shale* from Messel, Germany.

Methods: Samples collected using organically-clean techniques underwent pyrolysis at a 1mg:1µL ratio with TMAH. The fatty acids were analyzed by pyro-GCMS using either a SAM-like pyrolysis oven ramp (35 °C/min) or a flash pyrolysis at 500 °C on a Frontier pyrolyzer coupled to either an Agilent or Thermo GC-MS instrument.

Results: Results of the SAM-like and flash pyrolysis oven method analyses techniques are compared below.

SAM-like Pyrolysis. Using the SAM-like pyrolysis ramp, low molecular weight (LMW) (C₈-C₁₀) FAMES were present in other samples, medium MW (MMW) (C₁₁-C_{18,2}) FAMES were present in select samples (Table 1), and high MW (HMW) (C₂₀-C₃₀) FAMES were detected in the shale sample only (not all data shown).

Flash Pyrolysis. Using the flash pyrolysis method, FAME detection was improved in all samples. Low and medium molecular weight FAMES were present in all samples, and high molecular weight FAMES were detected in the circumneutral lake sediment, active and inactive Icelandic hot springs, modern carbonate and sulfate salts, modern carbonate ooids, and the shale sample.

Discussion: In general, the flash pyrolysis method yielded more FAMES than the SAM-like oven ramp method for all samples. Interpretations of note are discussed below:

Iron Oxides. The number of FAMES detected in the modern acidic iron oxide sample was lower than expected for a modern microbial community. The low FAME detection in the older acidic Iron Mountain iron oxide may be due to a decreased microbial population within the rocks, or a reduction in FAME preservation due to the presence of iron oxides [3]. Within the Western Australia lake deposits, which also host phyllosilicates, the acidic sample yielded fewer FAMES than the circumneutral sample with both pyrolysis methods. The circumneutral sample had much better preservation of FAMES over the acidic sample, suggesting that lipid preservation is improved in circumneutral iron oxides + clay environments than in acidic iron oxide + clay environments. In addition, HMW FAMES were also detected in the circumneutral lake sediments, indicating a terrigenous plant or algal origin [4, 5].

Siliceous Sinter. The active hot spring surface sample contained 12 to 15 FAMES depending on pyrolysis method. A 4cm deep subsurface sample contained 9 to 10 FAMES depending on pyrolysis method (data not shown). Mono- and polyunsaturated fatty acids (MUFAs and PUFAs, respectively) were sometimes detected in the subsurface, indicating improved preservation and/or lack of early degradation of the FAMES.

The inactive hot spring surface sample contained 5 to 11 FAMES depending on pyrolysis method. A 7 cm deep subsurface sample contained 2 to 9 FAMES depending on pyrolysis method (data not shown). MUFAs and PUFAs were not detected in the subsurface, indicating rapid degradation of the unsaturated FAMES, either via microbial heterotrophy or diagenesis [6].

Carbonate & Sulfate Salts. The salts were located within a ~2ka lava tube that is compositionally closest to martian basalts. With the flash pyrolysis method, the carbonate salts (calcite, magnesite, hydrocalcite), contained 16 FAMES and the carbonate and sulfate salts (thermo-

natrite, burkeite, trona) contained 10 FAMES. These data are consistent with detection of FAMES in a modern community via MTBSTFA pyrolysis and DNA sequencing [7].

Carbonate. The modern ooids contained 4 to 15 FAMES depending on pyrolysis method. The SAM-like detection represented a very small fraction of the lipids present in these ooids [8].

Shale. The Messel shale contained 22 to 35 FAMES depending on pyrolysis method, including 11 HMW FAMES. HMW FAMES are most consistent with plant and algal origins [8], and the lipids in the Messel Shale have a demonstrated algal origin and strong lipid signal [9].

In situ experiment. Fatty acids are detectable and possibly preferentially preserved in clay mineralogies, even if mixed with iron oxides from Mars-analog environments. Similar mineralogies are anticipated to be encountered in the “phyllosilicate trough” south of the Vera Rubin Ridge on Mt. Sharp. The rover is expected to soon explore this cryptic ‘clay-bearing’ unit which will provide an ideal opportunity to perform the SAM TMAH experiment. Several potential locations have been identified which will enable sampling of substrate that 1) is rich in clays (based on identification via CRISM spectra), 2) at the stratigraphic lowest point in the clay unit along the rover’s anticipated traverse, and 3) may have been more recently exposed near an eroding southern scarp of the Vera Rubin Ridge [10].

Conclusions: These experiments demonstrate that TMAH thermochemolysis with a SAM-like pyro-GCMS is effective, and FAMES have been detected in Mars-analog samples that vary in mineralogy, age, and microbial community input. Fatty acids are detectable and possibly preferentially preserved in clay mineralogies, even when mixed with iron oxides. Similar mineralogies are anticipated to be encountered in the “phyllosilicate trough” south of the Vera Rubin Ridge on Mt. Sharp. Laboratory experiments using the other SAM wet chemistry reagent, MTBSTFA, are ongoing on the same set of martian analogs. This method will allow us to compare the number of fatty acids detectable with MTBSTFA and TMAH to better understand the efficiency of both reagents. Future high fidelity experiments will include MTBSTFA to understand any effects of MTBSTFA chemistry on thermochemolysis and the interpretation of the data. This research enhances the ability of SAM to characterize organic compounds and identify potential organic biosignatures in Gale Crater.

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