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Diverse Organic Molecules on Mars Revealed by the first SAM TMAH Experiment

Amy Williams¹, Jennifer L. Eigenbrode², Maëva Millan³, Ross Williams^{2,4}, Ophélie McIntosh³, Samuel Teinturier^{2,5}, Janelle Roach¹, Charles Malespin², Paul Mahaffy², Alexander B. Bryk⁶, Arnaud Buch⁷, Luoth Chou², Jason P. Dworkin², Valerie Fox^{8,9}, Heather Franz², Caroline Freissinet³, Daniel P. Glavin², Christopher H. House¹⁰, James M.T. Lewis^{2,11}, Angel Mojarro¹², Rafael Navarro-Gonzalez¹³, Chad Pozarycki², Andrew Steele¹⁴, Roger E. Summons¹², Cyril Szopa³, Ashwin Vasavada¹⁵; ¹Univ. of Florida (amywilliams1@ufl.edu), ²NASA Goddard Space Flight Center, ³LATMOS, ⁴Notre Dame Univ., ⁵USRA, ⁶Univ. of California, Berkeley, ⁷CentraleSupélec, ⁸Univ. of Minnesota, ⁹Caltech, ¹⁰Pennsylvania State Univ., ¹¹Howard University, ¹²MIT, ¹³Universidad Nacional Autónoma de México, ¹⁴Carnegie Institution for Science, ¹⁵JPL

Introduction: The 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 [2]. SAM performs sample analysis via pyrolysis and gas chromatography mass spectrometry (GC-MS). SAM additionally performs wet chemistry experiments, either by *N*-methyl-*N*-(*tert*-butyldimethylsilyl)-trifluoroacetamide (MTBSTFA) derivatization or tetramethylammonium hydroxide (TMAH) thermochemolysis. Coupled with wet chemistry, the GC-MS can detect non- to semi-volatile organics (at standard conditions) that could derive from martian macromolecules, as occurs on Earth. The SAM TMAH experiment hydrolyzes molecules in drill samples, releasing them from their host macromolecules, and then through methylation renders them sufficiently volatile for detection by GC-MS [2]. This work reports on the results from the first *in situ* TMAH wet chemistry experiment conducted by SAM on Mars. Ongoing analyses indicate that the TMAH experiment was successful, and that a variety of aromatic molecules were generated. Some of these molecules *may* be indigenous to Mars whereas others are known to be produced by SAM.

Background: 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 μ L of TMAH in methanol (1:3 v:v) with pyrene and 1-fluoronaphthalene in solution used as recovery standards. Inside the cup is a second sealed reservoir filled with nonanoic acid that will react with TMAH when the reservoir is punctured and serves as an additional internal calibration standard.

The first TMAH wet chemistry experiment on Mars was performed in September 2020 at the Mary Anning (MA) drill site in the Glen Torridon region [3]. The drill site was selected based on anticipated mineralogic similarity to the Glen Etive drill site, which would prioritize abundant clay minerals and minimal iron oxide phases. A location that was substantially stratigraphically below the diagenetically altered material near the contact with the Greenheugh pediment was also desired to limit the impact of alteration on the sample site [4].

Methods: Six sample portions were delivered to a punctured SAM TMAH cup. The sample was saturated with TMAH from the cup and raised into the pyrolysis oven. A split of the volatiles released from pyrolysis was monitored by the quadrupole mass spectrometer (QMS) for the entire temperature ramp for evolved gas analysis (EGA). For GC-MS, the volatiles released during pyrolysis were diverted through the SAM hydrocarbon trap under He flow as cuts at selected temperature intervals. The cut from >560°C was sent only to the QMS for EGA. Volatiles trapped on the SAM hydrocarbon trap were released by heating the trap to ~300 °C and then split between GC1 (MXT-20) and GC2 (MXT-5) chromatographic channels for their separation.

Results: Engineering data indicate the TMAH cup was punctured and powdered sample from the MA drill hole delivered. Trimethylamine byproduct masses from the TMAH reaction were detected. The 1-fluoronaphthalene recovery standard was also identified, but not the nonanoic acid and pyrene standards. ‘Bands’ of masses grouped together and having mass-to-charge (*m/z*) 190 to 485, represent high molecular weight molecules detected by the SAM QMS. These data indicate that large, complex molecules were present. A variety of methylated, oxygen-, sulfur-, and nitrogen-bearing aromatic organics were detected in GC-MS and/or EGA data. The possible origin(s) of these molecules are discussed below.

Discussion: The successful first *in situ* TMAH experiment demonstrates that a variety of organic molecules can be liberated by the SAM TMAH experiment.

A) Organics detected in EGA and GC-MS. Some of the molecules that were identified in both the EGA and GC-MS data may be indigenous to the sample, as opposed to being SAM-internal byproducts. This interpretation is still being assessed. Examples of molecules identified in both EGA and GC-MS include benzene, toluene, trimethyl- and tetramethyl-benzene, naphthalene, and methylnaphthalene. TMAH has a basic pH and is a methylating reagent that enhances the cleavage of ester bonds and methylates pyrolysis products *in situ*. The presence of methylated single and two-ring aromatics suggests that these organics might derive from a macromolecular source that was cleaved and

methylated by TMAH thermochemolysis. We note that with limited TMAH reagent, no TMAH blank was conducted, so we cannot rule out carry over from previous analyses.

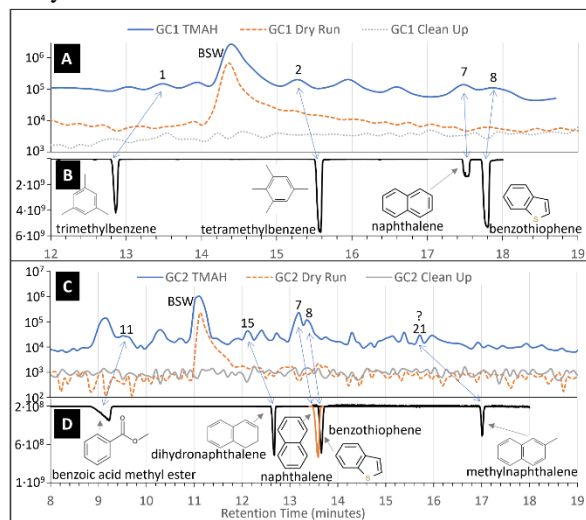


Figure 1. GC1 and GC2 chromatograms (A & C) and laboratory benchtop retention time experiments (B & D) confirm the identification of trimethylbenzene, tetramethylbenzene, methylbenzoate, dihydronaphthalene, naphthalene, and benzothiophene in the Mary Anning TMAH experiment. Methylnaphthalene is likely, thus marked with the '?'. Lines represent summed m/z 120, 121, 128, 130, 134, 135, 136, 140, 142, 144, 148, 149, and 150. In A & C, solid blue line is the TMAH experiment, dashed orange line is the 'dry run' analysis performed prior to the TMAH experiment (same conditions as the experiment but without a sample or TMAH), dotted gray line is the post-TMAH experiment clean up analysis. In B & D, black and orange lines represent molecular standards analyzed on the relevant SAM-like instrument on-GC1 and GC2 columns. BSW - bisilylated water.

B) Organics detected with GC-MS only. Molecules detected only with GC-MS may be either indigenous to the sample or be formed from reactions with TMAH within the SAM gas processing system (e.g., reactions with Tenax in the hydrocarbon trap or with the column stationary phase). Examples of the organics detected in GC-MS only analyses include trimethyl- and tetramethylbenzene, naphthalene, benzothiophene, dihydronaphthalene, and methylnaphthalene (Fig. 1). Benzoic acid has been detected with SAM from both Mars-indigenous [5-7] and SAM-internal [7,8] sources. The benzoic acid methyl ester therefore results from the reaction of TMAH methylating benzoic acid of indeterminate source.

Thiophene has been previously detected on Mars with SAM in addition to other sulfur-bearing organics [3,9] and the benzothiophene detection is likely Mars-indigenous. These molecules were not methylated but may have been liberated from a macromolecular source by the TMAH reaction.

C) SAM-internal organics. Several known SAM-internal molecules were identified in the EGA and GC data, including mono- and bisilylated water from

reactions between water and MTBSTFA, and dimethylsilanediol-2-*t*-BDMS from the reaction of MTBSTFA with the GC column. Aromatic byproducts detected here and associated with the reaction of MTBSTFA with the hydrocarbon trap Tenax include benzene, toluene, 1-ethynyl-3-methylbenzene, benzoic acid, naphthalene, and diphenylmethane [8]. Although benzene, toluene, and naphthalene are listed here as SAM-internal byproducts, this is not necessarily the source of these molecules in the EGA data.

Sources of organics. Meteoritic input is one possible source of organics on the martian surface. Several organics identified with the TMAH experiment were also liberated from the Murchison meteorite with SAM-like TMAH thermochemolysis benchtop experiments, including toluene, trimethylbenzene, methylnaphthalene, and benzothiophene [10]. During TMAH thermochemolysis, the Murchison insoluble organic matter is degraded into its constituent parts, some of which are detectable with GC-MS. Molecules detected with neat pyrolysis of Murchison included benzene and naphthalene [11].

Amines and amides were not prevalent in Murchison pyrolysate [12]. However, UV irradiation experiments of benzene and naphthalene in the presence of water and NH_3 -containing ices can generate dihydronaphthalene [13]. It is therefore possible that UV irradiation has contributed to radiation processing of meteoritic organics.

TMAH methylates carboxylic acids with high efficiency. Carboxylic acid methyl esters (CAMEs) have been generated from TMAH thermochemolysis of Murchison [10]. The lack of CAMEs in these data suggest that 1) CAMEs are not present in amounts detectable with SAM or 2) flight operating conditions require optimization before they can be detected clearly.

Conclusions: This study documents the first *in situ* TMAH wet chemistry experiment on Mars, which was performed by the SAM instrument aboard the Curiosity rover. This study has identified over 20 aromatic molecules with methyl, methylamine, ether, alcohol, and ester/carboxylic acid functional groups, sulfur-, and potentially nitrogen-bearing organics. Both one and two ring aromatics have been identified. We propose that this suite of organics represents TMAH thermochemolysis breakdown products from ancient organic macromolecular material that has been preserved in billions-of-years-old sedimentary rocks in Gale crater.

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