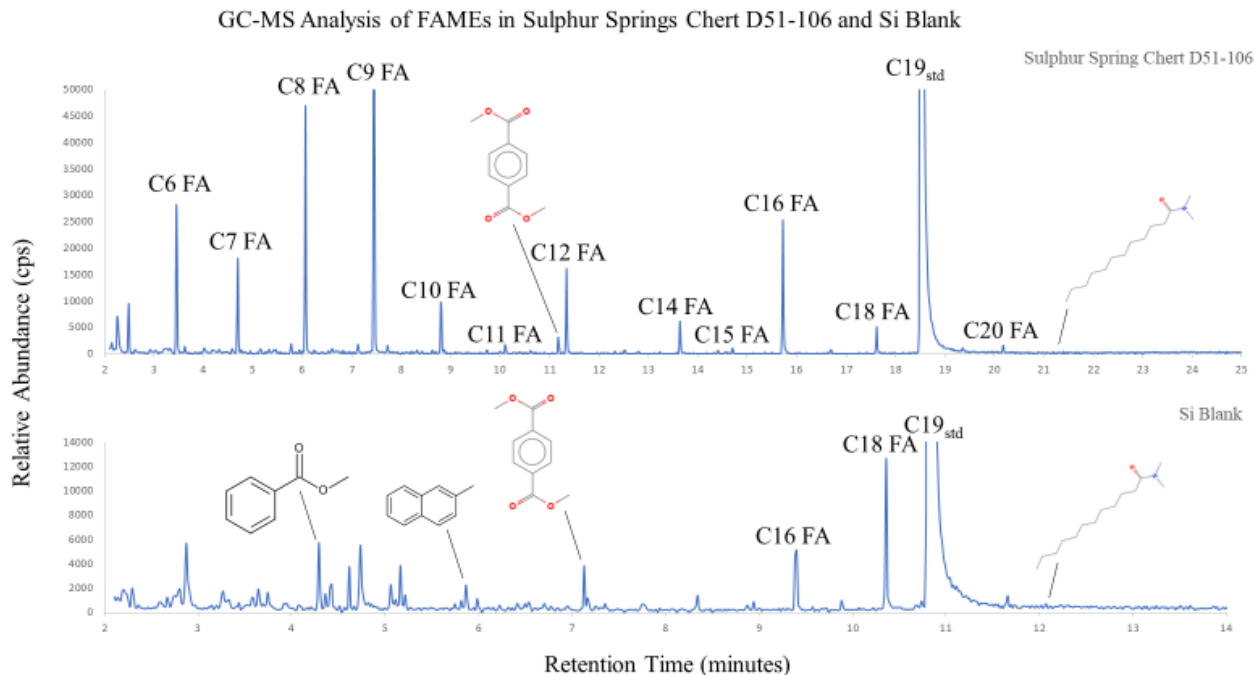


**ORGANICS DETECTION IN ANCIENT CRATONIC ROCKS WITH TMAH WET CHEMISTRY.** H. O. Boles<sup>1</sup>, A. J. Williams<sup>1</sup>, D. Oehler<sup>2</sup>, <sup>1</sup>Department of Geological Sciences, University of Florida ([hboles@ufl.edu](mailto:hboles@ufl.edu)), <sup>2</sup>Planetary Science Institute.



*Figure 1. Chromatographs of the 3.24Ga Sulphur Springs Group chert vs fused Si blank analyzed with TMAH thermochemolysis.*

**Introduction:** In the astrobiology community, natural terrestrial samples provide important proxies for testing and validating organics detection strategies. However, a challenge with many Mars analogs is that samples are often geologically young. The majority of Mars' surface is more than 3.5 billion years old [1], so it brings into question how valid these young Mars analogs are. In this study, a suite of Precambrian, cratonic rock samples from a variety of locations on Earth are used as Mars analogs to understand (1) how ancient cratonic samples respond to tetramethylammonium hydroxide (TMAH) thermochemolysis, and (2) how successful a TMAH thermochemolysis experiment on ancient Martian bedrock might be.

NASA's *Curiosity* rover landed on Mars in 2012 and it contains the Sample Analysis at Mars (SAM) instrument suite. A gas chromatograph - mass spectrometer (GC-MS) was included in the SAM instrument suite and one of its purposes is to analyze Martian sediments for organic molecules. Also included in the SAM suite are two metal wet-chemistry cups loaded with TMAH [2]. TMAH thermochemolysis is a reagent that can liberate organics bound in macromolecules thereby making them more volatile and detectable by the GC-MS [3].

Thirteen samples from the Canadian, South African, and Australian cratons are studied here to evaluate the

efficacy of biomarker liberation by SAM-like TMAH thermochemolysis. The samples used in this study have experienced little to no metamorphism, a process which would destroy the organics we look for during geochemical analysis. They also represent a wide temporal (1.1 – 3.4 Ga) as well as environmental (marine, black smoker, hydrothermal, and banded iron formation (BIF)/lacustrine) range.

In this study, TMAH thermochemolysis is used to liberate any carboxylic acids present in the cratonic rock samples and convert them to fatty acid methyl esters (FAMES) that are amenable to GC-MS detection. Flash pyrolysis is used to detect alkanes and alkenes. This study focuses on detecting alkanes, alkenes, and fatty acids as it has been documented that microbial communities on Earth show a preference toward odd-over-even hydrocarbon chain length and even-over-odd fatty acid chain length [3]. Therefore, these patterns widely qualify as biosignatures throughout astrobiological studies.

**Methods:** Each of the 13 samples had pebble-sized pieces broken off using a rock hammer and an ashed (500°C for 8 hours) chisel. The pebble-sized pieces broken off of the original sample were then ground with an ashed mortar and pestle to achieve a mixture of 3-5 mm pieces.

Residual surface organics were then removed from the mixture via solvent washing and sonication. To do this, each mixture was placed in a 100 mL beaker, submerged in methanol, and sonicated for 10 minutes. The methanol was then decanted, and each mixture was re-submerged in dichloromethane (DCM) and sonicated again for 10 minutes. The DCM was decanted and the process was repeated with fresh DCM and 5 minutes of sonication until no suspended particles were observable in the solvent. Once the solvent had no observable suspended particles, 1 mL of solvent was transferred to a solvent-washed vial using a sterilized pipette and then placed in refrigerated storage. Each now-washed mixture was transferred to a sterilized Whirl-Pak and stored at room temperature.

Once all samples had been surface solvent washed, the samples were then powdered using a ball mill. The ball mill headset was solvent washed with methanol and DCM and then ashed. After ashing the headset, an ashed silica gel blank was put in the ball mill headset and powdered. The powdered silica gel was then collected using an ashed metal scoop and placed in a solvent-washed vial. The headset was then solvent washed again with methanol followed by DCM. Once the headset was dry, the sample was transferred into the headset from its Whirl-Pak and powdered. The powdered sample was then collected using a new ashed metal scoop and placed in a solvent-washed and ashed vial. Both the powdered silica gel and sample vials were then stored at room temperature. This process was then repeated for every sample.

After powdering, samples were analyzed with a Frontier Multi-Shot (EGA/PY303D) pyrolyzer and an Agilent 7890B GC-5975C XL inert MSD GCMS. Each sample was prepared in two different ways: simple pyrolysis for alkane/alkene analysis and TMAH thermochemolysis for fatty acid analysis.

**Simple pyrolysis preparation:** A solvent-washed spatula was used to load 3-5 mg of powdered sample into a sterile pyrolysis cup. 1.5  $\mu$ L of C<sub>19</sub> fatty acid was injected in each cup as the internal standard.

**Thermochemolysis preparation:** A second set of samples were prepared identically. A solvent-washed spatula was used to load 3-5 mg of powdered sample into a sterile pyrolysis cup. 1.5  $\mu$ L of C<sub>19</sub> fatty acids was injected in each cup as the internal standard. In addition, 1  $\mu$ L of TMAH to every 1 mg of sample was injected.

**GC-MS:** Samples analyzed for alkanes/alkenes were pyrolyzed at 600°C for 0.5 min. The oven program ramped from 70°C to 300°C at 20°C/min with a 10 minute hold. Samples analyzed for fatty acids were subject to the same pyrolyzer and oven programs as for alkanes/alkenes. Molecules were identified based on

retention time and fragmentation pattern using Chem-Station software.

**Results and Discussion:** TMAH thermochemolysis was performed on Sulphur Springs Chert D51-106 and its Si blank. This sample comes from the 3.24 Ga Sulphur Springs Group black smoker deposit in Australia. This sample contains organic matter as bundles of filamentous and tubular structures that resemble modern microbial body forms that have not experienced alteration temperatures >100°C [4]. The sample was collected from diamond drill coring from a depth of 703.5m. *Figure 1* illustrates the resulting chromatographs. Multiple molecules were similar between the Si blank and Sulphur Springs Chert D51-106. These peaks were identified as C<sub>16</sub> fatty acid (FA), C<sub>18</sub> FA, benzenedicarboxylic acid dimethyl ester, and dimethyldodecanamide. The C<sub>16</sub> FA was detected at a higher relative abundance in Sulphur Springs Chert D51-106 while the C<sub>18</sub> FA was detected at a higher relative abundance in Si blank. Both FA are common contaminants from cellular membranes.

Both the benzenedicarboxylic acid dimethyl ester and the dimethyldodecanamide were detected at approximately equal relative abundances. Other molecules detected and identified from Sulphur Springs Chert D51-106 were: C<sub>6</sub> FA, C<sub>7</sub> FA, C<sub>8</sub> FA, C<sub>9</sub> FA, C<sub>10</sub> FA, C<sub>11</sub> FA, C<sub>12</sub> FA, C<sub>14</sub> FA, C<sub>15</sub> FA, and C<sub>20</sub> FA. The total organic carbon (TOC) in Sulphur Springs Chert D51-106 is 1.73%, the highest of this sample suite, and may reflect the elevated organics detected in the sample. Other molecules detected and identified from the Si blank were benzoic acid methyl ester and methyl-naphthalene. Determination of the source of these aromatics is ongoing.

**Conclusion:** There are several FAs in the sample that were absent in the blank, lending confidence that they are native to the sample. However, the even-over-odd FA carbon number preference may indicate a modern microbial community. The source of these FAs and aromatic organics continues to be under investigation.

**Future Work:** Further analysis will be performed on the broad range of samples in our suite of Precambrian rocks having varying mineralogies, ages and TOC%.

**References:** [1] McKay C.P. and Stoker C. R. (1989) *Reviews of Geophysics* 27(2), 189-214. [2] Mahaffy P.R. *et al* (2012) *Space Sci Rev* 170, 401-478. [3] Williams, A. J. *et al* (2019) *Astrobio* 19(4), 522-546. [4] Duck, L.J. *et al* (2007) *Prec Res* 154, 205-220.