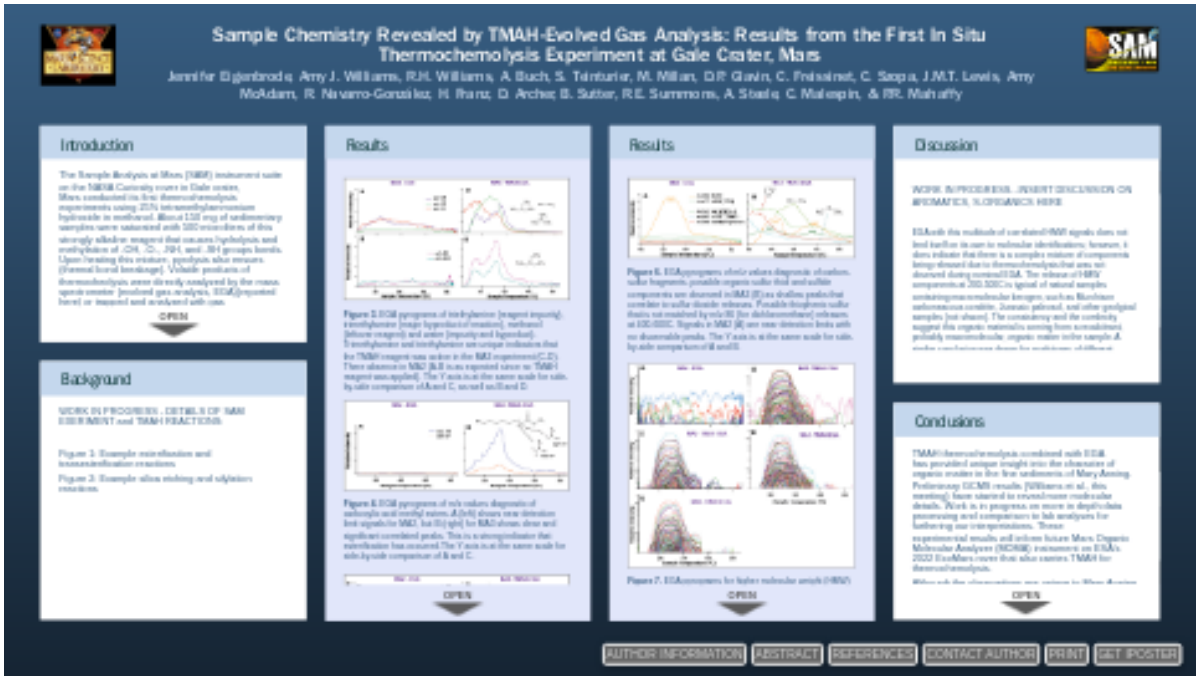
Sample Chemistry Revealed by TMAH-Evolved Gas Analysis: Results from the First In Situ Thermochemolysis Experiment at Gale Crater, Mars



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UPDATED ABSTRACT

The Sample Analysis at Mars (SAM) instrument suite on the NASA Curiosity rover in Gale crater, Mars conducted its first thermochemolysis experiments using 25% tetramethylammonium hydroxide in methanol. About 150 mg of sedimentary samples were saturated with 500 microliters of this strongly alkaline reagent that causes hydrolysis and methylation of -OH, -O-, -NH, and -SH groups bonds. Upon heating this mixture, pyrolysis also ensues (thermal bond breakage). Volatile products of thermochemolysis were directly analyzed by the mass spectrometer (evolved gas analysis (EGA); reported here) or trapped and analyzed with gas chromatography mass spectrometry (GC-MS; see Williams et al, this meeting).

Importantly, TMAH us stringly alkaline and releases organic components bound to both minerals and other organics (within macromolecules, such as kerogen, humic substances, or biomolecules). Together, these actions have the potential to release diverse inorganic and organic chemicals from sedimentary samples that are not observable by other SAM experiments.

This report focuses on the EGA associated with the first TMAH thermochemolysis experiment on the Mary Anning target a phyllosilicate-bearing sedimentary sample from the Glen Torridon region (see McAdam et al, Sutter et al, and Byrk et al, this meeting for sample composition and geological provenance). EGA-TMAH results indicate the experiment was successful and revealed a greater abundance and diversity of molecules were released using TMAH as compared to nominal EGA under He. Importantly, the sedimentary organic material gave rise to a wide array of high molecular weight fragments, which suggest recalcitrant organic material likely of macromolecular nature.

BACKGROUND

No sole technology distinguishes all organic molecular components in biological, geological, or meteoritic samples because naturally occurring molecules have different chemistries (e.g., polar vs. non-polar, low to high molecular weight) and are packaged within inorganic materials in a variety of ways (i.e., organics may be bonded, absorbed or trapped by minerals, liquids, gases, or other organics). Structurally and chemically complex macromolecules (e.g. biopolymers, large biomolecules, humic substances, kerogen) make up more than 90% of organic matter in most natural samples on Earth and in meteorites. In geological and meteoritic samples, macromolecules are a common intermediate and end product of post-formation and post-depositional processes that tend to generate more recalcitrant components. Such processes are responsible for preservation of organic materials in the terrestrial rock record. Methodologies that tap the molecular information contained within macromolecules is critical to both the detection of extraterrestrial organic matter and understanding the processes the led to its presence.

Thermochemolysis using 25% tetramethyl ammonium hydroxide (TMAH) in methanol reagent followed by in-line analysis via gas chromatography mass spectrometry (GCMS) is one such method. Also referred to as thermally assisted hydrolysis and methylation (THM), it is commonly used to break ether and ester bonds of biologically derived material to produce volatile methylated products that are detectable by GCMS (Robb and Westbrook, 1963; Challinor 2001, Williams et al., 2020); though it is also known to attack carboxylic acid, ketone, aldehyde, amine, thiol and hydroxy groups. The analytical approach has been used to provide a general characterization of organic matter chemistry but has also specifically employed to investigate lipids (triglycerides, phospholipids, cholesteryl esters, free fatty acids), lignin phenols of plants, proteinaceous materials including peptides and amino acids, and recently, nucleobases (Hedges and Mann, 1979, Clifford et al., 1995, Knicker et al, 2001; Hendricker et al, 1998; Gallois et al 2007; He et al., 2019). TMAH-thermochemolysis is conducted at temperatures ranging from 250°C (Zang et al., 2001; Watson et al, 2010; Challinor 2001) up to ~600°C (Remusat et al., 2005), though the TMAH-induced transesterification of free fatty acids reaction can occur as low as 60°C (Alcantara et al., 2000; Cerce et al., 2005).

TMAH is suitable for Martian materials for other reasons. As it is reactive in the presence of low percentages of salts (e.g. perchlorate) (Mißbach, et al. 2019) and water. It is corrosive to silicates with inactive (Si-H) and active (Si-OH) sites, thereby disrupting bonds between organic molecules and minerals.

The broad applicability of TMAH thermochemolysis to both characterize organic matter composition and potentially reveal detailed chemistry of molecular components bound in macromolecules or to mineral surfaces, including multiple types of biomolecules, makes it promising method for exploring organic matter on other planets and moons (Eigenbrode et al., 2011; Williams et al, 2019, He et al. 2020).

WORK IN PROGRESS

Figure 1: Example reaction scheme showing TMAH reaction with amino, carboxylic acid and hydroxyl groups (from Zang et al., 2001).

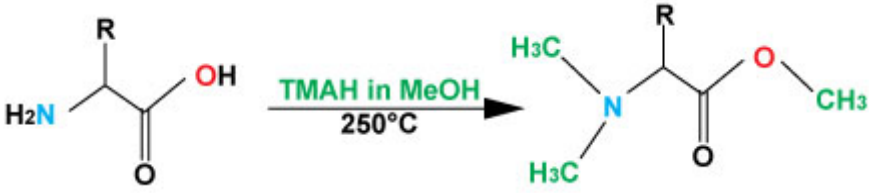
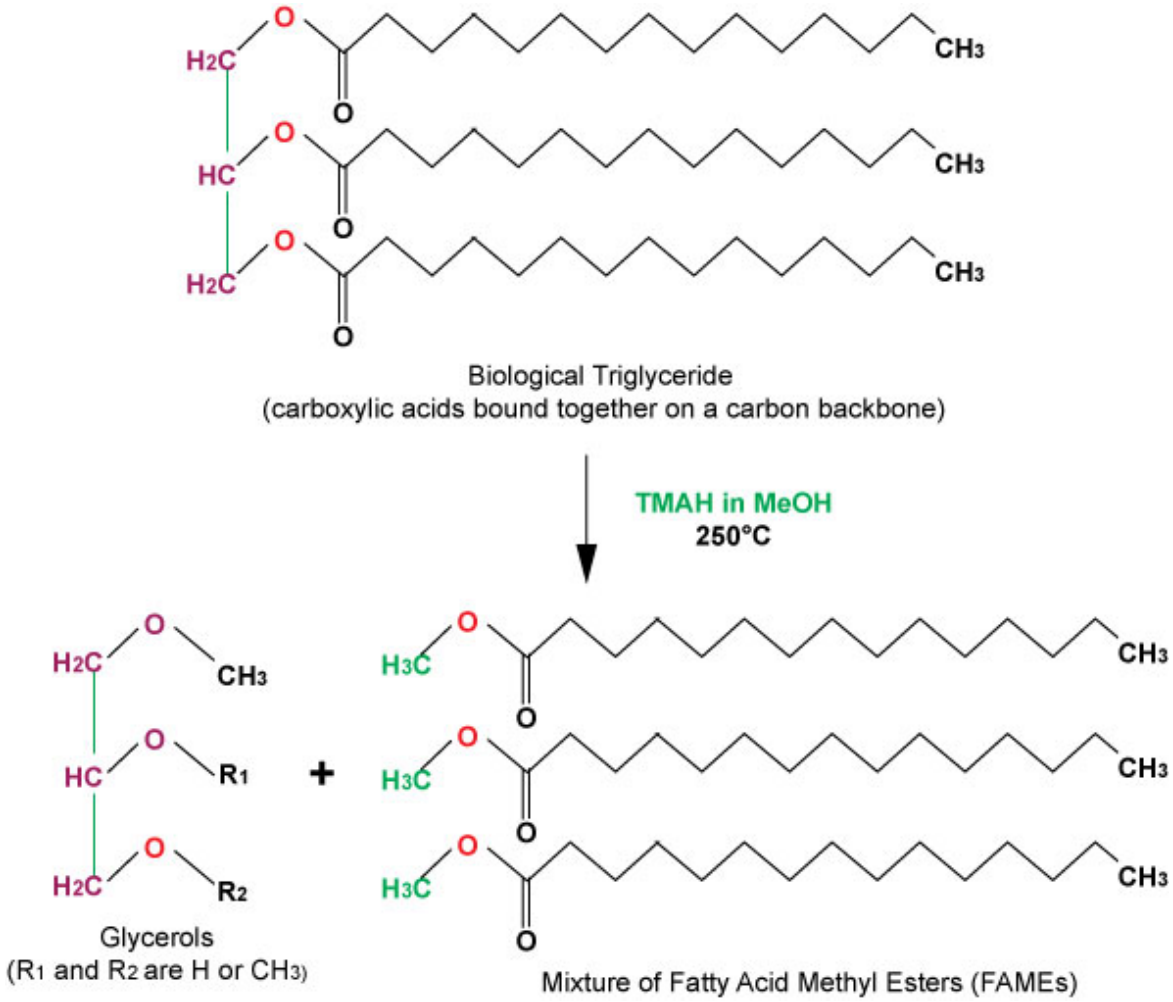


Figure 2: Example transesterification reaction scheme showing TMAH reaction with carboxylic acids bound together by a carbon backbone (triglyceride) that gets cleaved from the backbone during hydrolysis and then methylated resulting in products that are volatile for gas analysis


Biological Triglyceride
(carboxylic acids bound together on a carbon backbone)
TMAH in MeOH
250°C
Glycerols
(R1 and R2 are H or CH3)
Mixture of Fatty Acid Methyl Esters (FAMEs)

RESULTS

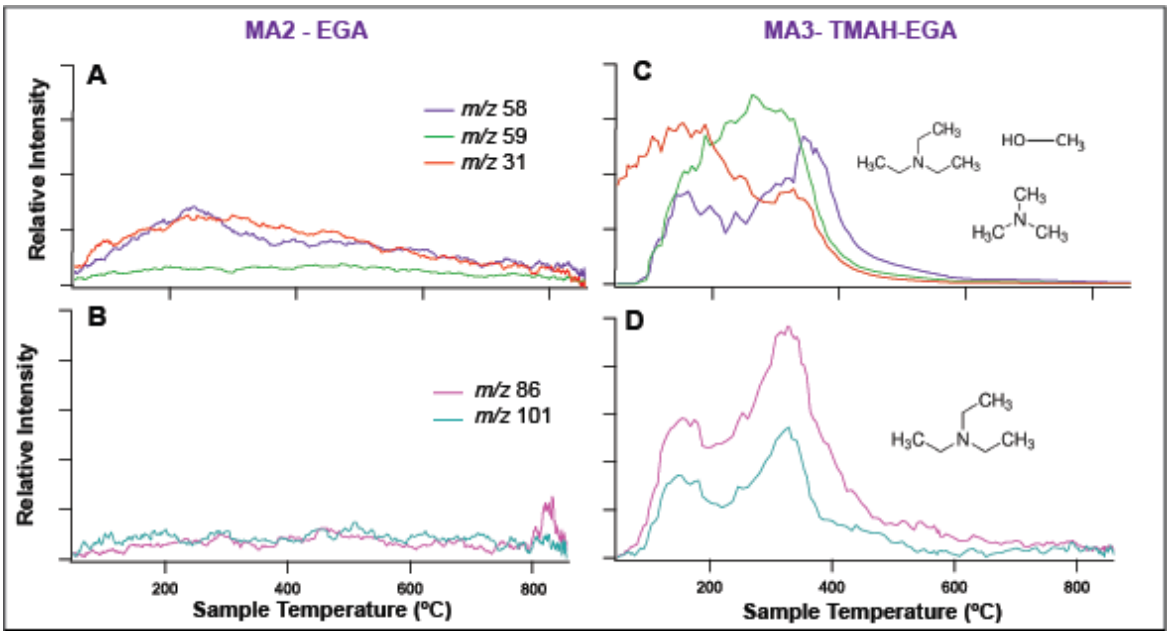


Figure 3. EGA pyrograms of triethylamine (reagent impurity), trimethylamine (major byproduct of reaction), methanol (leftover reagent) and water (impurity and byproduct). Trimethylamine and triethylamine are unique indicators that the TMAH reagent was active in the MA3 experiment (C-D). There absence in MA2 (A-B is as expected since no TMAH reagent was applied). The Y axis is at the same scale for side-by-side comparison of A and C, as well as B and D. *m/z* = mass to charge ratio

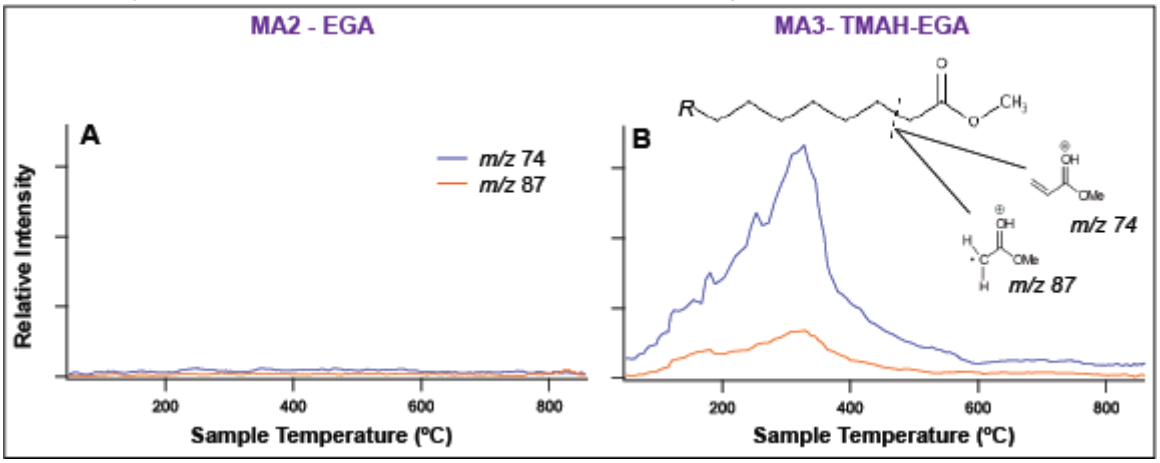


Figure 4. EGA pyrograms of *m/z* values diagnostic of carboxylic acid methyl esters. A (left) shows near detection limit signals for MA2, but B (right) for MA3 shows clear and significant correlated peaks. This is a strong indicator that esterification has occurred.The Y axis is at the same scale for side-by-side comparison of A and C.

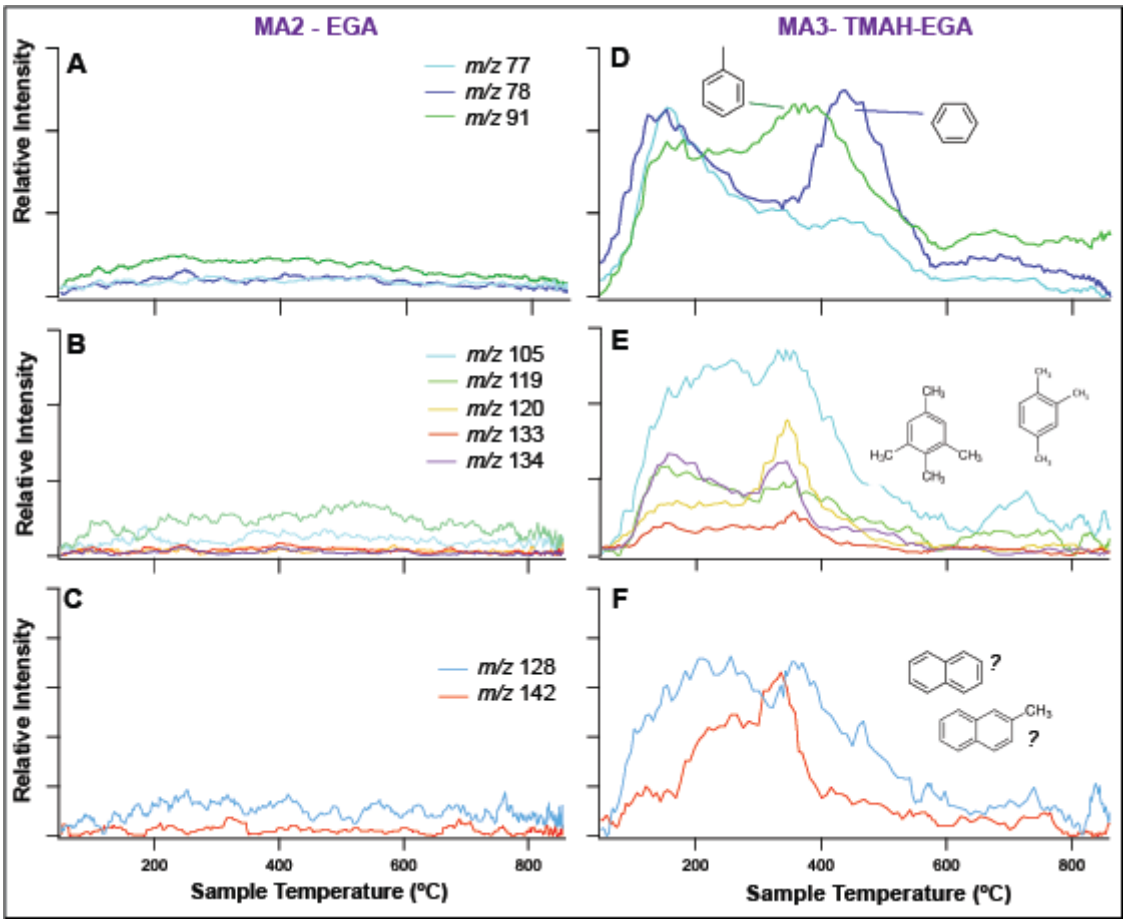


Figure 5. EGA pyrograms of *m/z* values diagnostic of simple single ring aromatics (A,D), methylated benzenes (B,E), and double ring aromatics including a methylated version (C,F). THe lack of peaks suggestive of aromatics in MA2 sharply contrasts to the peaks observed in MA3 after thermochemolysis. Methylated aromatics may be reaction products of the TMAH thermochemolysis and some have been observed in GCMS (see Williams, et al, this meeting). The Y axis is at the same scale for side-by-side comparison of A and D, B and E, as well as C and F.

RESULTS

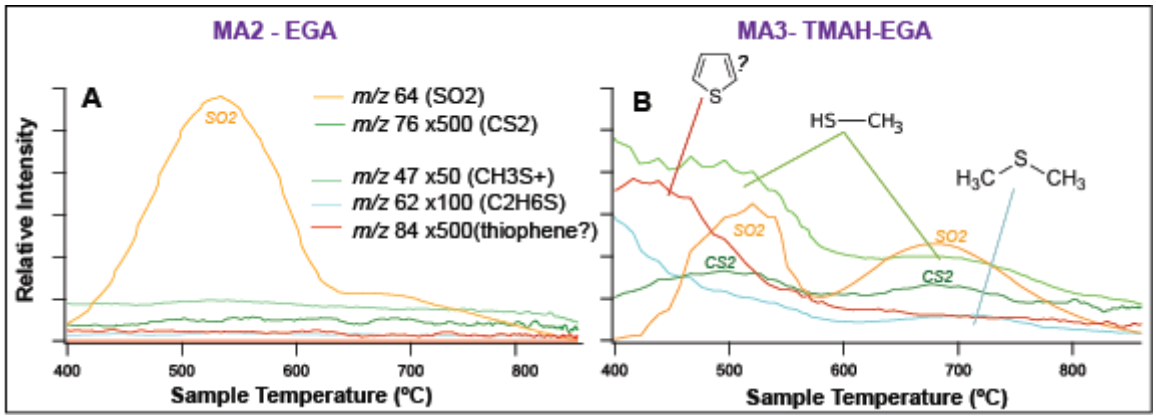


Figure 6. EGA pyrograms of *m/z* values diagnostic of carbon-suflur fragments. possible organic sulfur thiol and sulfide components are observed in MA3 (B) as shallow peaks that correlate to sulfur dioxide releases. Possible thiophenic sulfur that is not matched by *m/z* 86 (for dichloromethane) releases at 400-600C. Signals in MA2 (A) are near detection limits with no discernable peaks. The Y axis is at the same scale for side-by-side comparison of A and B.

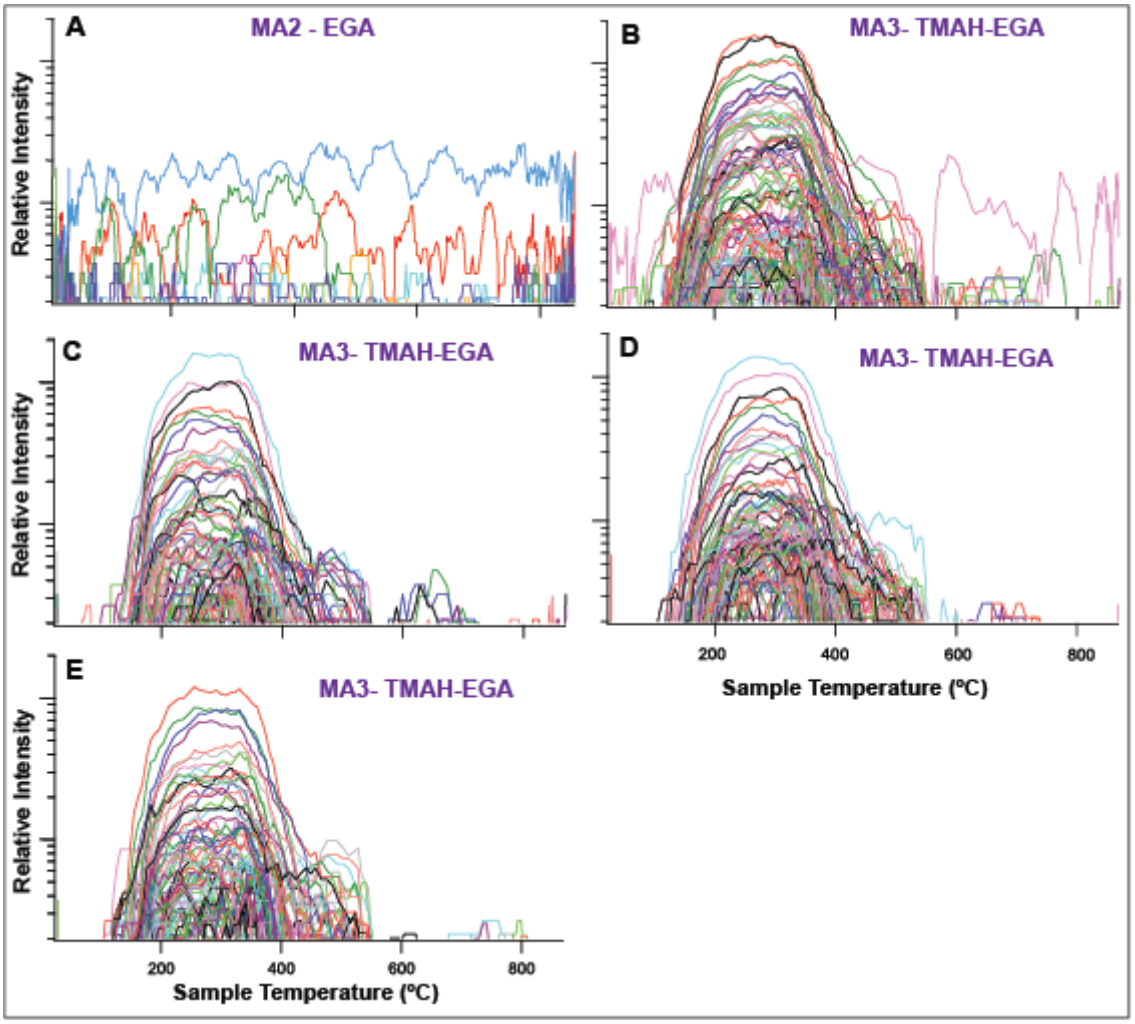


Figure 7. EGA pyrograms for higher molecular weight (HMW) m/z values indicating fragments from molecules larger than simple aromatic, aliphatic, or organic S components. In A for MA2, *m/z* 151-537 is plotted, but most signals were below detection. In contrast, MA3 thermochemolysis generated a vast array of HMW signals as 1 main peak with possibly two smaller releases at higher temperature. MA3 pyrogram sets asr B: *m/z* 151-250, C: *m/z* 251-350, D: *m/z* 351-450, and D: *m/z* 451-537. The Y axis is logarithmic and at the same scale for all 5 plots.

DISCUSSION

The suite of EGA pyrograms showing the multitude of correlated high molecular weight (HMW) signals (Fiure 7) does not lend itself on its own to molecular identifications; however, it does indicate that there is a complex mixture of components being released from the Mary_Anning sample due to thermochemolysis that was not observed during nominal EGA. The release of HMW components at 200-500°C is typical of natural samples containing macromolecular kerogen, such as Murchison carbonaceous chondrite, Jurassic paleosol, and other geological samples (not shown). The consistency and the *m/z* diversity of pyrogram signals suggest this organic material is coming from a recalcitrant, probably macromolecular, organic matter in the sample. A similar conclusion was drawn for mudstones of different chemical composition at the base of the Murray formation (Eigenbrode, et al., 2018) but based on different results.

The significant release of aromatic components with TMAH in comparison to normal pyrolysis (Figure 5) likely reflect both the thermochemical breakup of molecular components that are either bound to each other by TMAH-targeted functional groups or are polar free molecules in the sample. Aromatic compounds may be due to a combination of aromatics in the Mary_Anning organic material or aromaticity that occured during thermochemolysis.

EGA data for organic-sulfur volatiles shows more varied release associated with inorganic S volatiles as compared to S-volatiles observed in normal pyrolysis. It is not clear what feature(s) of the sample may be driving this disparity.

Of note, aliphatic signals are not clearly detectable in EGA data due to strong contribution of TMAH pyproducts to the low molecular mass signals that aliphatic detections depend upon.

CONCLUSIONS

TMAH thermochemolysis combined with EGA has provided unique insight into the character of organic matter in the fine sediments of Mary Anning. Preliminary GCMS results (Williams et al., this meeting) have started to reveal more molecular details. Work is in progress on more in depth data processing and comparison to lab analyses for furthering our interpretations. These experimental results will inform future Mars Organic Molecular Analyzer (MOMA) instrument on ESA's 2022 ExoMars rover that also carries TMAH for thermochemolysis.

Although the observations are unique to Mary Anning at the top of the Murray formation, the interpretation is consistent with that for mudstones at its base (Eigenbrode et al., 2018). Organic material in these mudstones is refractoryt to the geological processed that degrade it. Such processes include mutiple episodes of groundwater related diaagenesis and exposure to oxidants and ionizing radiation for 10s to 100's of millions of years. The persistance of organic material in up to 3.6 billion year old lake sediments that have been exposed to radiation, points to the possibility of better preservation in mudstones that have not been exposed. Both NASA's 2020 Perserverence rover, which will seek out recently exposed (scarp related?) outcrops, and ExoMars rover, which will drill 1-2 m deep below most of the penetrating ionizing radiation may encounter organic-bearing mudstones from ancient habitable environments and uncover more details of its molecular story.

AUTHOR INFORMATION

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ABSTRACT

The Sample Analysis at Mars (SAM) instrument suite on the NASA Curiosity rover in Gale crater, Mars has the capability to conduct wet chemistry experiments, including two thermochemolysis experiments. In these experiments, 50-150 mg of sedimentary samples bearing diverse minerals and chemical compositions, including possible organic materials, will be saturated with 500 microliters of 25% tetramethylammonium hydroxide [TMAH] in methanol. Upon heating this mixture, the alkaline reagent methylates amenable functional groups (via hydrolysis of -OH, -O-, -NH, and -SH groups followed by methylation) to produce volatile products that are directly analyzed by the mass spectrometer (evolved gas analysis, EGA) or trapped and analyzed with gas chromatography mass spectrometry (GC-MS). Importantly, the TMAH reagent is corrosive to silicates with active -OH sites and releases organic components bound to both other organics (within macromolecules) or minerals. Together, these actions have the potential to release diverse inorganic and organic chemicals from sedimentary samples that are not observable by other SAM experiments. The search for long-chained carboxylic acids is enabled by this experiment (see Williams et al., this meeting). There is also the potential for a unique and more diverse organic chemistry to be revealed that may shed light on organic chemical sources, preservation mechanisms and degradation processes. In particular, functionalized aromatics and small organic acids, which were observed in other SAM experiments and are possible radiolysis/oxidation products of ancient deposited sedimentary organics, may be detected in greater abundance. Current Mars Science Laboratory (MSL) mission's SAM results will inform future Mars Organic Molecular Analyzer (MOMA) analyses involving TMAH thermochemolysis of 3.9-billion-years-old, clay-rich samples collected by the 2022 ExoMars rover from the surface to 2-meters depth in the Oxia Planum region. This report will focus on the evolved gas analysis associated with the first TMAH thermochemolysis experiment (to be conducted on Mars in 2020) on a phyllosilicate-bearing sedimentary sample from the Glen Torridon region. Results will be compared to other SAM experiments and include related GCMS observations.

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