Investigating the Organic Chemical Evolution of Enceladus Recorded by the Macromolecular Organic Matter from Its Plume

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NO PHOTOS

Exploring planetary OCE

Habitability, biological potential, and possible ecology at any point in time and space are all dependent on the organic chemical evolution (OCE) of a planet and its environments (Davila and Eigenbrode, 2024). However, organic molecules that are the direct products of abiotic, prebiotic, or biotic formation processes are subject to transformation by the environment that can preserve, degrade, or otherwise complicate the original record of formation. Missions that aim to search for molecular signatures of life that are organic in nature will also likely be capable of exploring aspects of a planetary body's OCE.

Macromolecules in the Enceladus Plume

At Enceladus, Cassini's Cosmic Dust Analyzer (CDA) measured the composition of icy grains as the Cassini spacecraft passed through the plume of ocean materials exhausting from the South Polar Terrain. At 20-50 km altitude, 40-60% of plume ice grains were rich enough in organics to enable instantaneous detection (i.e., without bulk sample collection) (Postberg et al., 2018). CDA measurements detected mass fragments up to 2100 Da mass, characterized by abundant H-unsaturation (double bounds, aromatics), O-bearing, and N-bearing functionality indicating functionalized macromolecules. They are hypothesized to be products of enrichment at the ice-crust/ocean-water interface (Porco et al., 2017; Postberg et al., 2018), where cold temperatures would slow further reactions.

Type 2 grains in the plume containing the high mass organic cations (HMOC) identified and interpreted as macromolecules. The HMOC spectral signature showed repeating peaks in the bulk mass spectra separated by 12-13 amu in the 8—200 amu range. Khawaja et al. (2019) compared HMOC to insoluble organic matter (IOM) of carbonaceous chondrites.

This Study

Here we explore analog macromolecules using a different technique than Cassini's CDA. The CDA relied on hypervelocity impact (>5 km/s) to fragment and ionize organic components as they entered the instrument, thus providing an instantaneous bulk measurement of the total composition. In this laboratory study, we investigate macromolecular IOM isolated after multiple solvent extractions and standard fulvic acid isolation methods. IOM samples were then subjected to thermally assisted hydrolysis and methylation (THM) using two reagents:

1) 25 wt% Tetramethylammonium hydroxide in methanol (TMAH)

2) 0.25M Trimethylsulfonium hydroxide in methanol (TMSH)

THM was conducted in a pyrolyzer operated at 260C connected to a gas chromatograph mass spectrometer.

These experiments serve to:

- Shed light on the Cassini observations relative to a range of materials having different, known OCE qualities
- Compare TMSH and TMAH reagents efficiency on analog IOM
- Demonstrate the potential of these methods to reveal diverse compounds in IOM that might reveal detailed chemistry to help evaluate the OCE status of Enceladus' Ocean – a prime target for an astrobiology mission (NASEM, 2023)

What is THM?

TMSH methylates -COOH, -O-, -SH, aromatic-OH, ring-NH2 groups of heterocycles functional groups, while TMAH also methylates aliphatic-NH2, aromatic-NH2, of aliphatic-OH. Both are widely used for the detection of compounds in a wide variety of natural materials of biological, geological, and meteoritic affinity. TMAH (25%) is strongly alkaline (pH 13) and is a more robust hydrolysis reagent than 0.25 M TMSH (pH 9). With sufficient hydrolysis, macromolecules can loosen up, allowing more labile components that may or may not be bound to release upon heating. (This is demonstrated by the high boilers, including an Fe-chelated compound (*), in the fulvic acid (Fig. 1F), but also the biological samples (Fig. 1 G,H). TMSH is a gentler reagent effective at releasing the less stable compounds and is better at preserving unsaturation (He et al., 2019).

Conclusions

Results suggest that both abiotic meteoritic like IOM and aqueously altered organic macromolecules, such as microbial dissolved organic matter of the Pony Lake Fulvic Acid Isolate, may produce the spectral patterning observed in Cassini CDA data.

Both TMAH and TMSH THM-GCMS have merits in accessing macromolecular components for identification and thus enabling evaluation of the OCE at Enceladus.

No planetary target destination or environment is without complications from processes that transform the molecular structures derived from formation processes. However, at Enceladus macromolecules in the plume are sufficiently abundant for detailed chemical and structural analyses based on Cassini's observations. Furthermore, organic molecules in the plume may be directly sourced from a modern habitable environment with the likelihood of minimal transformation over both time and space. As such, a future Enceladus mission has high probability of revealing details in an ocean beyond Earth, and the THM approach offers an effective method to access that chemical record.

Results

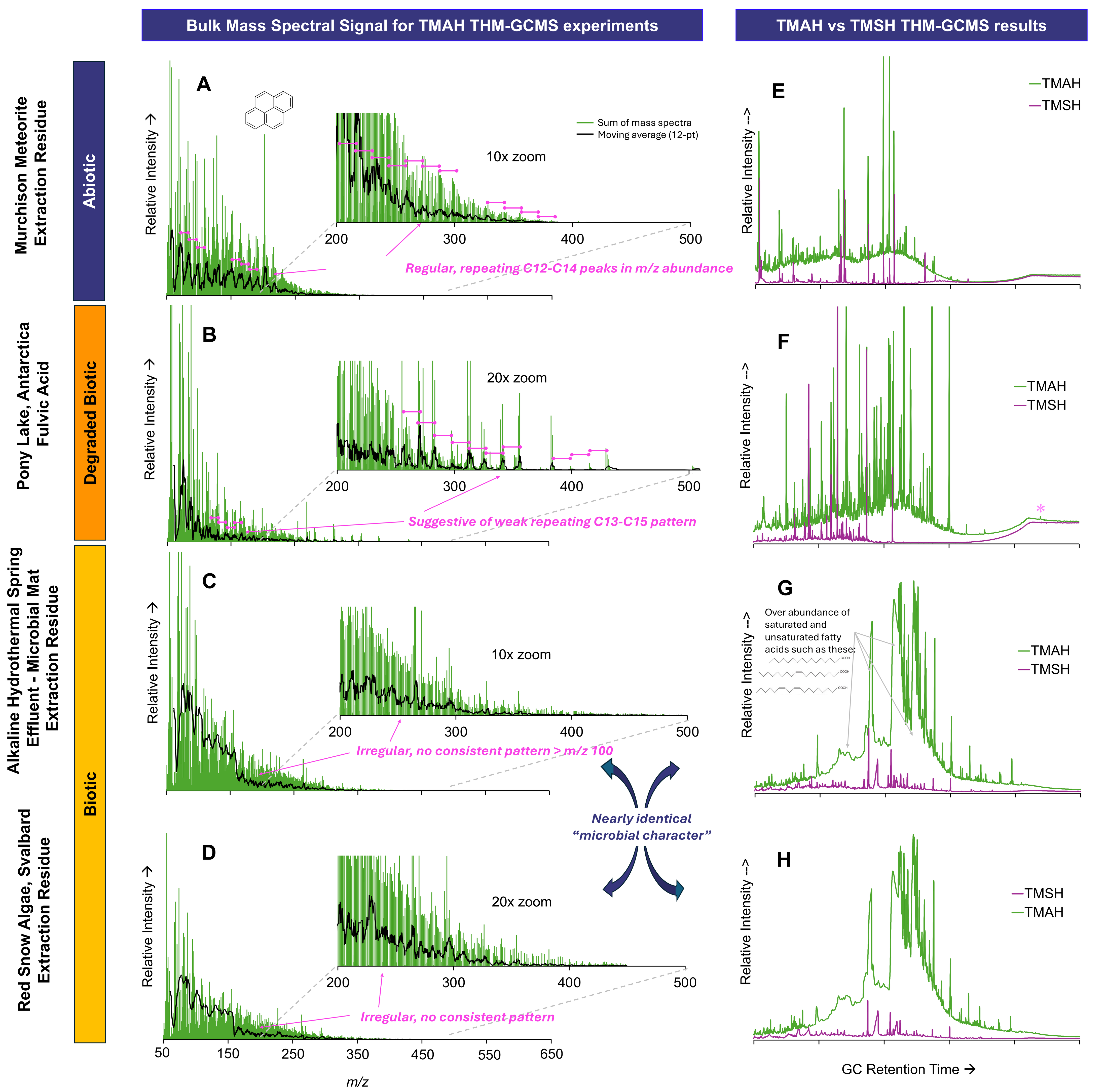

Figure 1. A-D: Bulk mass spectra summed over the majority of the chromatograms for TMAH experiments shows regular repeating pattern of C13-15 range in the (A) abiotic carbonaceous chondrite macromolecular organic matter, supporting the hypothesis that abiotic IOM are a possible source of the Cassini CDA observations for plume macromolecules (Khawaja et al, 2019), based on a spectra for all the macromolecular components that passed to the GCMS. In comparison, (B) environmentally reworked microbial material in the form of macromolecular fulvic acid (dissolved organic matter from the water column of Pony Lake, Antarctica; Cawley et al 2013) showed a similar, but much weaker pattern due to the presence of alkenes, ketones, and other functionalized sets of molecules, that largely include carbon chains. (C-D) Microbial and algal material from two uniquely different environments shows similar spectral character with no clear m/z patterning.

Figure 1. E-H: GC chromatogram comparison of TMAH and TMSH experiments for each sample. In all cases, TMAH yielded more diversity and quantity of molecules. All TMAH experiments resulted in an an unresolvable complex mixture that increase the background making identifications more labor intensive (requires careful background subtraction of spectra and greater dependence on retention time). TMSH experiments contain cleaner peaks for fewer compounds, but include more labile components (e.g., small acids) compared to the TMAH experiments. Detailed compositional analysis is in progress.

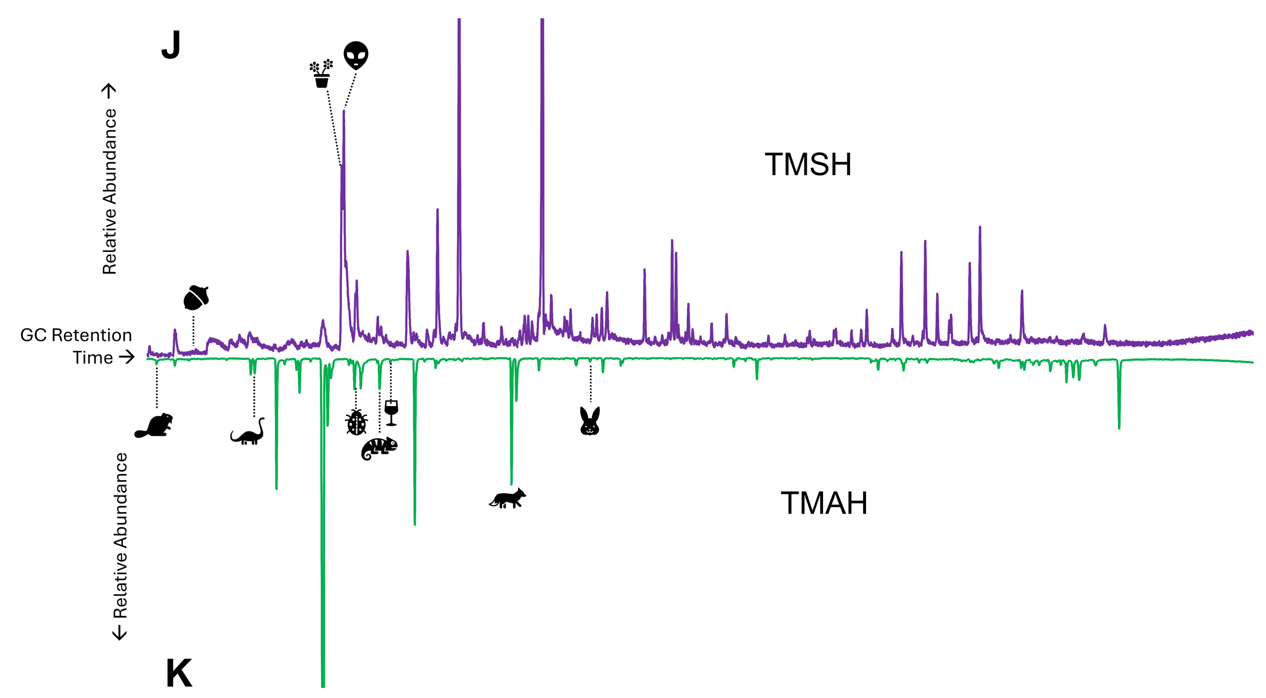

Figure 2 (J-K). Extracted ion chromatograms (sum of relevant m/z) for (J) TMSH and (K) TMAH THM-GCMS experiments of Angiotensin II human peptide standard. Preliminary results indicate the peptide underwent hydrolysis and methylation (symbols mark detected amino acid methyl esters), however there are other derivatives present under investigation. These results indicate that THM methods are capable of accessing amino acids in natural macromolecules (Boulesteix et al, 2023), interpretation of the derivatives may be challenging, especially when mixed with a array of other compounds as in Figure 1.

(Sum of m/z: 56, 56.1, 59, 60, 65.1, 68.1, 70, 72, 82.1, 87, 88, 91, 91.1, 102, 102.1, 103, 112, 112.1, 116, 117, 119.1, 120, 128, 129, 132, 133, 133.1, 134.1, 135, 144.1, 148, 148.1, 160, 162, 163, 171 and 192.1)

References

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