Characterizing Organic Matter from Biotic and Abiotic Sources via Laser Desorption Mass Spectrometry

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GEOL394

Introduction

- The Planetary Science and Astrobiology Decadal Survey has prioritized understanding:
  - Abiotic processes & their signatures
  - What the biosignature potential beyond Earth is
- This study focuses on three carbonaceous chondrites and three samples from the Marcellus Shale to characterize OM (organic matter) from abiotic and biotic sources
- Carbonaceous chondrites are the most carbon-rich meteorites, making them ideal candidates for study while the Marcellus Shale displays zones of thermal maturity, allowing for a more complete understanding of terrestrial OM & its breakdown

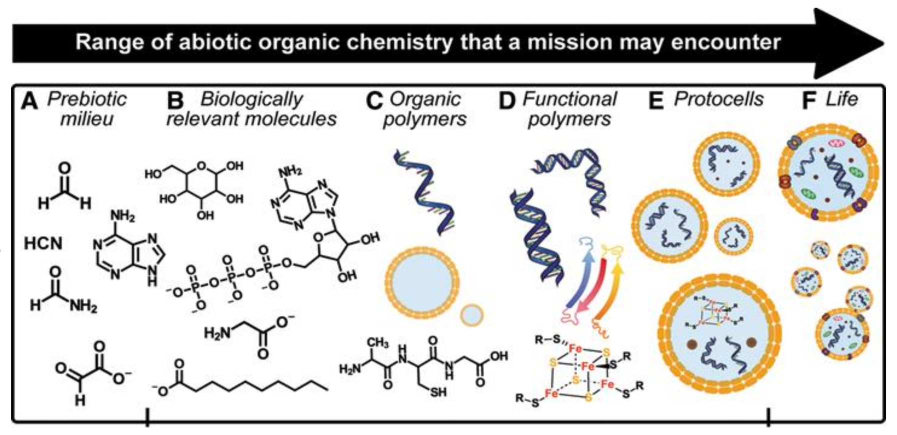

Figure 1: Schematic of increasing complexity of OM

Hypothesis

- Null Hypothesis 1: There is no statistically significant difference between biotic and abiotic OM based on chemical diversity, population distribution, & molecular structure
- Null Hypothesis 2: There is no statistically significant difference between OM in CM2 and C2-ung meteorites based on chemical diversity, population distribution, & molecular structure

Methods

- **Laser Desorption Mass Spectrometry (LDMS):** Ionizes & detects organic & inorganic signals in sample
  - **Mass Analyzer:** Thermo Fisher Q-Exactive Orbitrap
- **MFAssignR:** Open-source software, modified to fit the needs of the study. Assigns molecular formulas to each data peak

Procedures:

- Sample Preparation
  - Each sample was crushed (agate pestle) into ~silt-size grains between UHV foil
- 2 blanks were used: Clean Cu tape & UHV foil

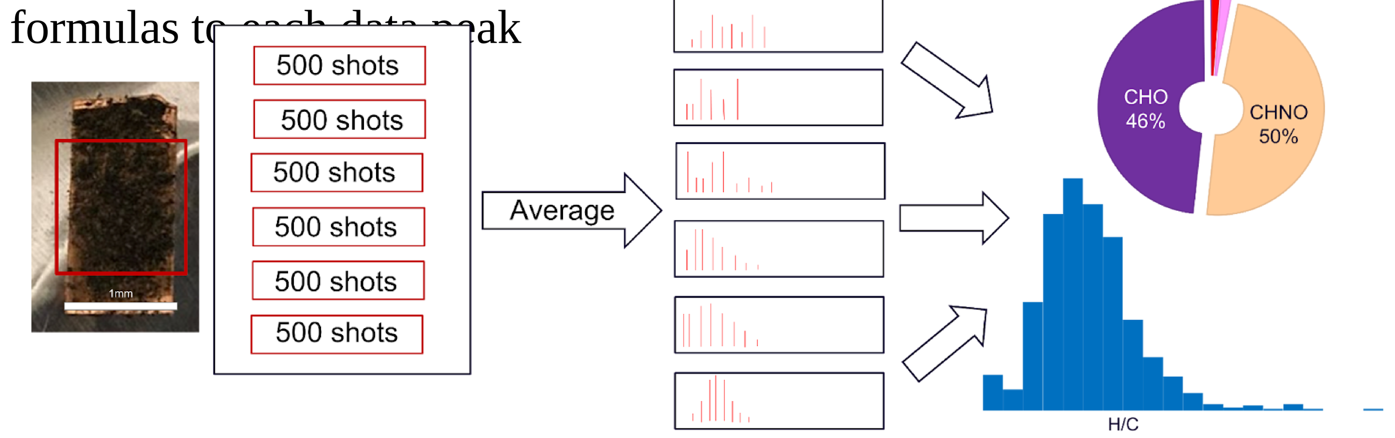

Figure 2: Schematic of how data was collected and processed

Results: Diversity

- **Heat maps are superimposed on van Krevelen Diagrams**
  - Used to assess origin & maturity of kerogen & petroleum
- Heat Maps: Created using the Kernal Density Estimation
- More compact "hot spots" approaching the y-axis (O/C<<1) likely indicate progressive degradation of organic matter
- Meteorites (except JW) show a much less degraded profile than Marcellus Shale

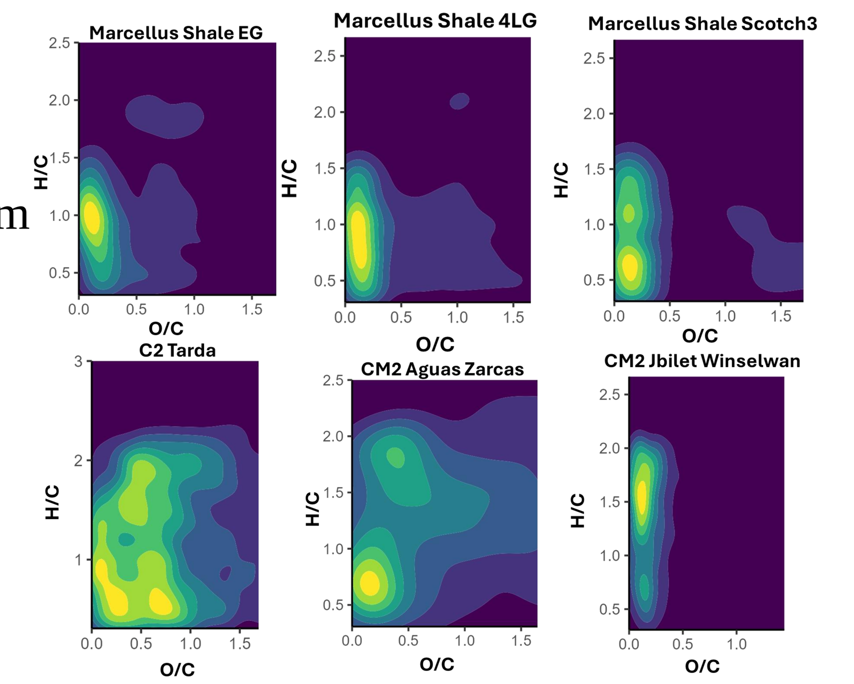

Figure 3: Heat maps ordered from least mature (left) to most mature (right). Shale samples on top, chondrite samples on bottom.

Results: Distribution

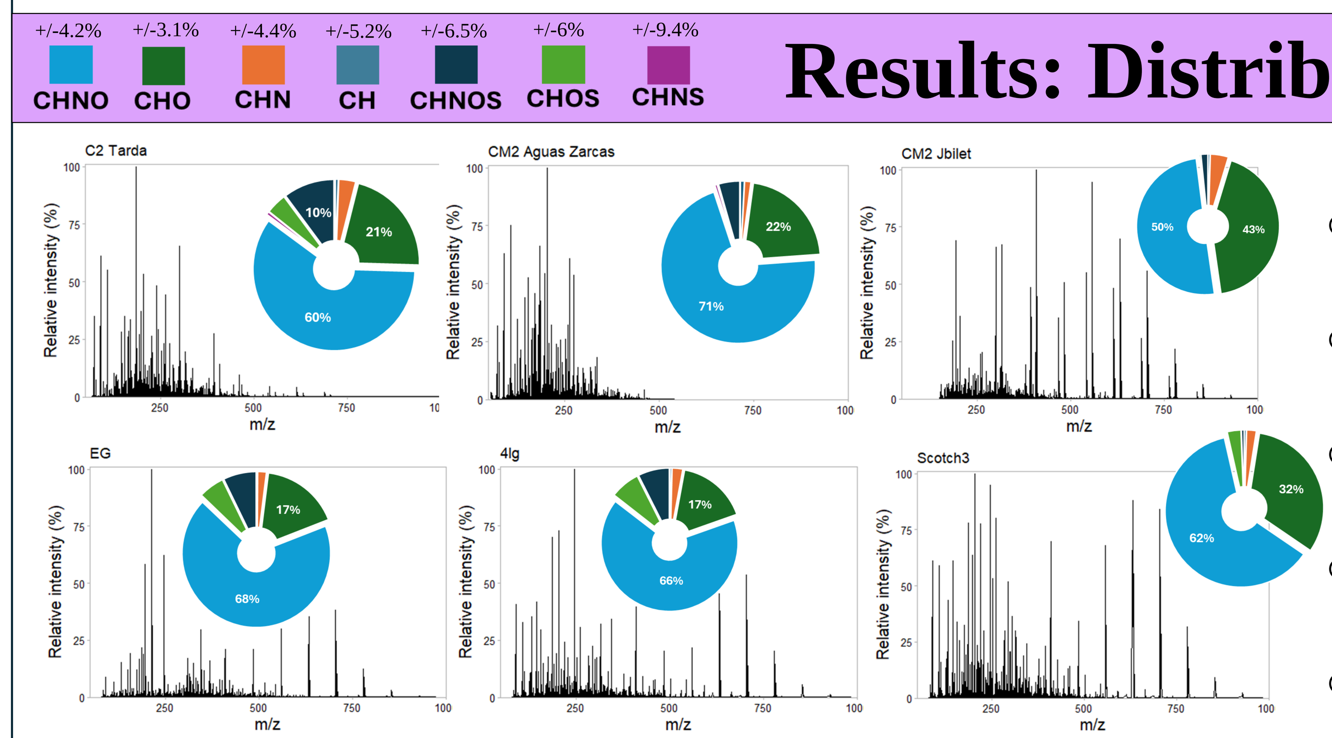

Figure 4: Mass spectra and donut plots for each sample. Donut plots represent the distribution of different formulas grouped by major elements

- Marcellus Shale showed higher concentration of high mass peaks → more complex OM
- JW shows distribution more consistent with Marcellus Shale than other meteorites
- Majority (~50-75%) of formulas are CHNO across all samples
- CHOS is much less prominent in chondrites compared to Marcellus Shale
- ~50-100% increase in CHO in JW & Scotch3 compared to other samples

Results: Structure

- **DBEO**: Double Bond Equivalence (including Oxygen)
  - Measures # of rings & double bonds in a molecular formula
  - Double bonds are stronger, shorter bonds
  - Can impact geometry of a molecule
- Mann-Whitney U Test:
  - Shale vs Chondrite: critical $p = 0.05$; calculated $p = 0.00$
  - CM2 vs C2-ung: critical $p = 0.05$; calculated $p = 3.41\times10^{-56}$
- Kruskal-Wallis Test:
  - Shale vs Shale: critical $p = 0.05$; calculated $p = 0.00$

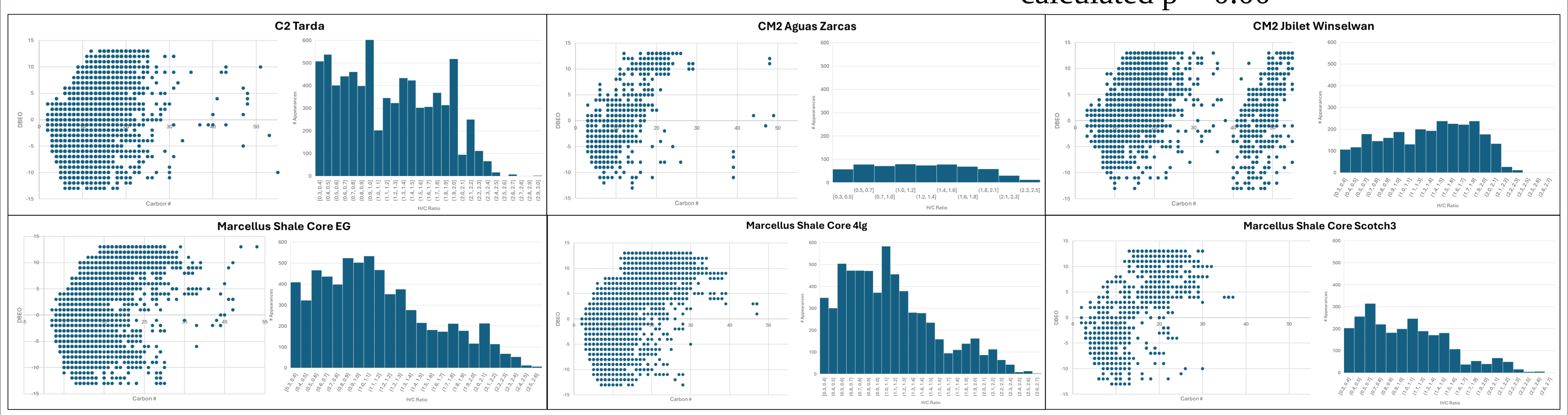

Figure 5: DBEO plot (left) and histogram (right) of each sample. Top row contains chondrite samples and bottom row contains Marcellus Shale samples

Discussion

- **Diversity:** Terrestrial samples indicate a sequence of OM degradation across samples, with the "hot spots" occurring near one another. Extraterrestrial samples are less consistent, with wider "hot spots" and no clear pattern among the three samples
- **Distribution:** Terrestrial samples show a comparative increase in high mass peaks (<500 m/z). They also contain a higher relative abundance of CHOS-group molecules.
- **Structure:** Terrestrial samples generally show a slightly more consistent preference for high (35-55) carbon numbers compared to extraterrestrial samples, which show a higher presence of high H/C ratios.
- Jbilet Winselwan is especially unexpected as its data appears to be more similar to the terrestrial samples rather than its fellow chondrites
  - A likely cause is terrestrial contamination. This sample is a find, not a fall, so it was more exposed to terrestrial material than the other chondrites (which are falls)

Conclusion

- Further work to classify & examine different terrestrial & extraterrestrial subgroups is necessary to fully understand any differences between the two groups.
- The difference in OM in abiotic and biotic samples is statistically significant, rejecting Null Hypothesis 1.
- The difference in OM between different abiotic samples is statistically significant, rejecting Null Hypothesis 2.

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