ANALYSES OF MOLECULAR AND COMPOUND-SPECIFIC C AND H ISOTOPIC RATIOS OF STEP-WISE THERMALLY DESORBED VOLATILE ORGANIC COMPOUNDS AND PYROLYSATES FROM MURCHISON AND AGUAS ZARCAS USING THE FRONTIER LAB DEVICE.

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Introduction: Step-wise thermal desorption and pyrolysis followed by gas chromatography–mass spectrometry (GC-MS) is among the simplest and least intrusive methods to characterize the organic composition of planetary materials such as meteorites or asteroid samples. The system can also be coupled to gas chromatography–isotope ratio mass spectrometry (GC-IRMS) for compound-specific isotopic analysis, which, for carbonaceous chondrites, offers important insights into the origin and synthetic pathways of various volatile and non-volatile organic components.

In this study, we employ a Frontier Lab 3030D Multi-shot thermal desorption and pyrolysis system coupled to GC-MS and GC-IRMS to analyze powder samples of Murchison and Aguas Zarcas. Our methodology differs from several recent studies [1,2] using the insoluble organic matter (IOM) because we directly analyze powdered meteorite samples. At low temperatures (e.g., < 200 °C), our system allows direct thermal desorption of existing volatile organic compounds with a minimal yield of pyrolysis products. At high temperatures (e.g., >400 °C), pyrolysis products from IOM dominate. Therefore, our methods allow the direct characterization of volatile, semi-volatile, and macromolecules efficiently and can be particularly informative for the comparison between different meteorites and asteroid Bennu obtained from OSIRIS-Rex mission [3].

Traditionally, IOM is extracted before analysis using acid digestion to remove mineral matrix [e.g., 1]. The yield of IOM is lower than 2 % (e.g., 0.5 % in reference [2]). However, pyrolysis GC-MS of IOM samples consumes 7 to 10 mg of IOM samples [1,2]. An important benefit to our technique is that the sample consumption is extremely small, e.g., milligrams of raw samples. This efficiency is important for valuable samples, such as those from asteroid Bennu that the OSIRIS-REx mission will deliver in September 2023 [3]. One of the key objectives of this study is to find out the minimum sample mass required for measurements of key compounds in Murchison using GC-MS and GC-IRMS so that we are fully prepared for the analysis of Bennu samples.

Results: For our analyses, we prepared an interior fragment of Murchison ME2644.26.92 from the Field Museum of Natural History. We carried out thermal desorption-pyrolysis of Murchison powder at seven temperature intervals with 20 min of holding time. During the thermal desorption and pyrolysis at each temperature interval, the evolved compounds are trapped in the column front with liquid nitrogen using the Frontier Lab Microjet cryotrap. GC-MS chromatograms of compounds produced at different temperatures are shown in Fig. 1, along with identifications for the key components. At a low thermal desorption temperature range (< 300 °C), we found a large number of relatively low-molecular-weight organic compounds including CO_2, toluene, isobutene, acetone, and carbon disulfide. Aromatic compounds (PAHs), including S-containing compounds, are found in pyrolysis temperatures from 200 to 500°C, such as thiophene, dibenzothiophene, and benzo[b]thiophene. Nitrogen-containing compounds are found mostly in the temperature range from 400 to 600°C, such as benzonitrile. The suite of compounds found in our experiments are very similar to those previously obtained by using 7 to 10 mg of Murchison IOM on a Frontier Lab model 2020iD instrument [1,2]. However, our GC-MS analyses require only 5 to 10 mg of Murchison raw powder. Considering that their IOM yield during sample preparation was ~0.5% of the bulk meteorite sample [2], the sample consumption of our analyses is lower by a factor of about 50 to 100.

Our results indicate that extracting IOM from bulk meteorite samples is likely unnecessary before thermal desorption and pyrolysis GC-MS analysis. Preparation of IOM removes volatile organic compounds, resulting in the loss of valuable information that can be obtained from direct thermal desorption. Pyrolysis of IOM appears to produce much lower amounts of pyrolysis products than from bulk raw samples (even though the diversity of compounds produced is similar). It is possible that macromolecules dispersed in the bulk meteorite mineral matrix may facilitate the breakdown of the macromolecules into GC-MS–amenable compounds. The harsh chemical treatment procedure to

make IOM could also inadvertently remove some organics. One other difference between ours and previous studies is that our Frontier Lab 3030D system has a built-in cryogenic system that allows pre-focusing of the compounds desorbed or pyrolyzed into the GC column, whereas the Frontier Lab 2020iD appears to lack column-front cryogenic focusing. Cryogenic focusing can greatly increase peak sharpness and detection sensitivity.

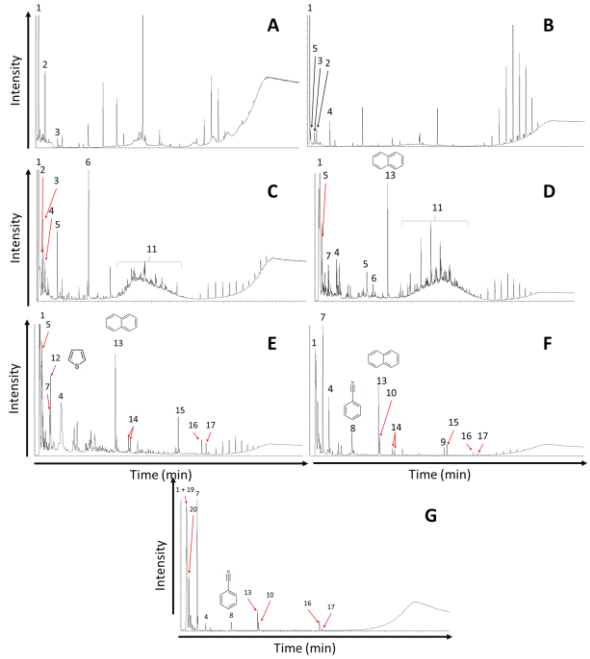

*Fig. 1. Total ions chromatograms of the gradual desorption and pyrolysis. (**A**) Temperature range: 50–100°C; (**B**) 100–150°C; (**C**) 150–200°C; (**D**) 200–300 °C; (**E**) 300–400°C; (**F**) 400–500°C; (**G**) 500–600°C. (1) CO_2 + SO_2; (2) n-hexane; (3) CS2; (4) toluene; (5) acetone; (6) dichlorobenzene; (7) benzene; (8) benzonitrile; (9) dibenzothiophene; (10) benzo[b]thiophene; (11) alkanes + alkenes; (12) thiophene; (13) naphthalene; (14) n-methylnaphthalene; (15) phenanthrene; (16) fluoranthene; (17) pyrene; (18) benzo[b]thiophene; (19) tetrafluoroethene; (20) H_2S.*

Conclusions: Direct thermal desorption-pyrolysis of raw meteorite samples provides a highly efficient molecular-level characterization of all indigenous organics (volatile and non-volatile compounds). The sample consumption is exceedingly small whereas the compound yields are extremely high, in comparison to published studies using IOM in thermal desorption and pyrolysis GC-MS. Cryogenic focusing allows greatly enhanced peak sharpness and chromatographic resolution, facilitating compound identifications and compound-specific isotopic analysis. Our approach allows us to rapidly establish the fundamental structural and isotopic profiles of a broad range of organics in different carbonaceous meteorites for comparison. We are performing more experiments to optimize the programs for thermal desorption and pyrolysis (steps and hold times and temperature range) on Murchison and will apply for our optimized programs to multiple meteorite samples, and eventually to samples from Bennu.

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