

CONVERSION AND EXTRACTION OF INSOLUBLE ORGANIC MATERIALS IN METEORITES. Darren R. Locke¹, Aaron S. Burton², and Paul B. Niles² ¹HX5 – Jacobs JETS Contract, NASA Johnson Space Center, Houston, TX (darren.r.locke@nasa.gov), ²NASA Johnson Space Center, Houston, TX

Introduction: We endeavor to develop and implement methods in our laboratory to convert and extract insoluble organic materials (IOM) from low carbon bearing meteorites (such as ordinary chondrites) and Precambrian terrestrial rocks for the purpose of determining IOM structure and prebiotic chemistries preserved in these types of samples. The general scheme of converting and extracting IOM in samples is summarized in Figure 1. First, powdered samples are solvent extracted in a micro-Soxhlet apparatus multiple times using solvents ranging from non-polar to polar (hexane - non-polar, dichloromethane - non-polar to polar, methanol - polar protic, and acetonitrile - polar aprotic). Second, solid residue from solvent extractions is processed using strong acids, hydrochloric and hydrofluoric, to dissolve minerals and isolate IOM. Third, the isolated IOM is subjected to both thermal (pyrolysis) and chemical (oxidation) degradation to release compounds from the macromolecular material. Finally, products from oxidation and pyrolysis are analyzed by gas chromatography - mass spectrometry (GCMS).

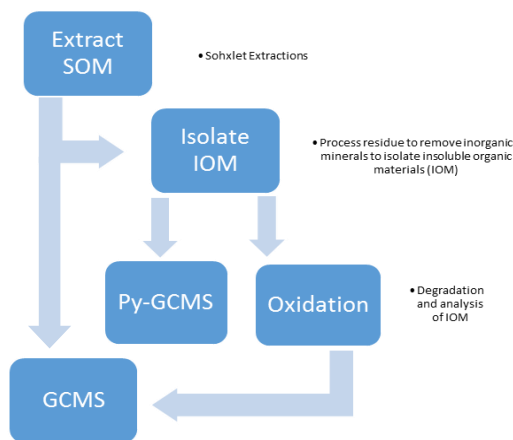


Figure 1. Generalized scheme for the conversion and extraction of IOM in meteorites and terrestrial samples.

Instrumentation and Methods: Micro-Soxhlet extractions remove soluble organic materials (SOM) from powdered meteorite samples loaded into high purity borosilicate glass fiber thimbles. Extraction is carried to completion and monitored by sampling aliquots of the solvents as a function of time and analyzing by GCMS. Demineralization (dissolution of inorganic minerals and other amorphous solids) of solvent

extracted samples are performed using strong acid (HCL and HF) washes (*e.g.* [1]).

The PY-GCMS system consists of a CDS pyroprobe (5200 model) coupled to a Thermo Trace-Ultra gas chromatograph with a Thermo DSQ II mass spectrometer. The GC column utilized for these studies is a 30m DB-5 (0.25 μ m film thickness and 250 μ m inside diameter). For a typical injection, the GC oven is ramped from 40 to 325 $^{\circ}$ C at a rate of 15 $^{\circ}$ C per minute and held at 325 $^{\circ}$ C for six minutes.

We utilize multiple pyrolysis procedures, including gradual, stepwise, and flash, and all these involve loading a small quantity (10-50mg) of powdered meteorite sample or isolated IOM into a glass capillary with glass wool to contain the sample. The loaded capillary is mounted into the pyroprobe platinum coil heater so that the coil windings encircle the entirety of the sample to be pyrolyzed. For stepwise pyrolysis, compounds will be released by heating to the desired temperature and holding for 10 minutes. Temperature steps are generally made at 100 - 200 $^{\circ}$ C intervals (*e.g.* 200 $^{\circ}$ C, 300 $^{\circ}$ C, 400 $^{\circ}$ C, 500 $^{\circ}$ C, 700 $^{\circ}$ C, 900 $^{\circ}$ C). During the duration of the heating, compounds are trapped in a tube containing Tenax-TA sorbent. Following heating, the compounds adsorbed on the Tenax-TA are thermally desorbed at 350 $^{\circ}$ C and injected, in one pulse, into the GC-MS for analysis. For flash pyrolysis, the tenax-TA sorbent trap is bypassed and the sample is heated to 610 $^{\circ}$ C or 900 $^{\circ}$ C nearly instantaneously and the pyrolysate is directly injected into the GCMS system for analysis. For gradual pyrolysis, the sample is heated from 100 $^{\circ}$ C to 1000 $^{\circ}$ C at 5 $^{\circ}$ C per minute, and the pyrolysate is transferred directly to the mass spectrometer through a deactivated metal capillary.

Results and Discussion:

We will concentrate our effort in this section to discussing stepwise Py-GCMS results on a sample of CM 1/2 ALH83100.

Gradual and stepwise pyrolysis have previously been used to study the IOM in meteorites such as the CM2 Murchison [*e.g.* 2]. Organic compounds that can be identified with these methods include both aliphatic and aromatic compounds. Aliphatic constituents may include normal, branched, and cyclic compounds, while

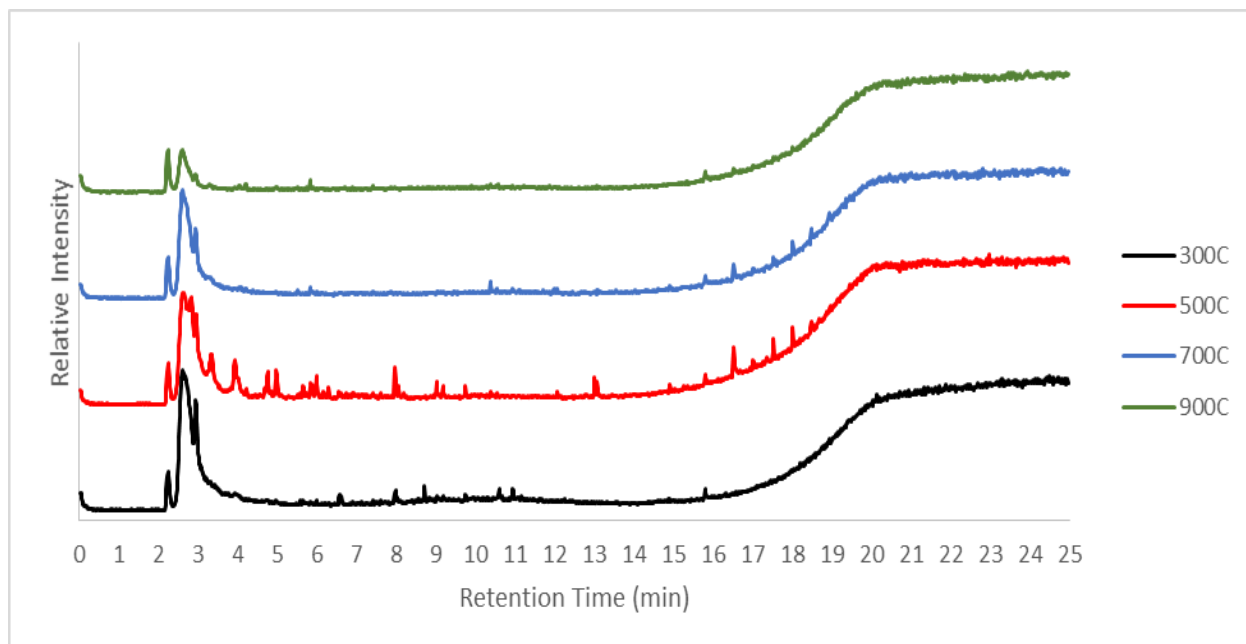


Figure 2. Stepwise pyrograms of CM 1/2 ALH83100.

aromatic constituents may include small one- to four-ring PAHs and associated alkylated compounds.

An example of a typical stepwise pyrolysis dataset we obtain from a CM 1/2 meteorite ALH83100, see Figure 2. This sample was subjected to stepwise pyrolysis at 300°C, 500°C, 700°C, and 900°C. Increasing temperature in a stepwise fashion provides qualitative information about the nature of the IOM, with compounds released at higher temperatures, requiring more energy to be released from the IOM. The stepwise pyrolysis of ALH83100 indicates that the majority of compounds are released below 700°C. These compounds include normal, branched, and cyclic aliphatic compounds and two to five ring poly-aromatic hydrocarbons and heteroatom (N, O, S) substituted species.

We have experimented with flash and stepwise pyrolysis of a polyaromatic hydrocarbon standard (Supelco PAH Mix 3) to determine the thermal stability of two to four ring compounds during pyrolysis. We found that these compounds were stable even under flash pyrolysis conditions at 900°C. No fragmentation of these compounds occurred during pyrolysis, giving us confidence that the aromatic compounds that we see in CM 1/2 ALH83100 are representative of compounds locked and then released from the IOM without thermal molecular reconfiguration.

Further, chemical degradation of the isolated IOM by ruthenium tetroxide preferentially destroys the aromatic compounds of the macromolecular structure and releases the intact aliphatic compounds; aliphatic products from this procedure are expected to be mono- and dicarboxylic acids that represent the linkages between poly-aromatic hydrocarbons that are interpreted to define the macromolecular structure of insoluble organic matter in some carbonaceous chondrites, including CM2 Murchison, and other types of meteorites [3]. We plan to utilize the scheme outlined in figure 1 to process samples to determine the prebiotic chemistry that ordinary chondrites and Precambrian terrestrial rocks contain.

Conclusions: We are working toward an integrated method and analysis scheme that will allow us to determine prebiotic chemistries in ordinary chondrites and Precambrian terrestrial rocks. Powerful techniques that we are including are stepwise, flash, and gradual pyrolysis and ruthenium tetroxide oxidation. More details of the integrated scheme will be presented.

References: [1] J. R. Cronin et al. (1987) *GCA*, 51, 299-303. [2] F. Okumura and K. Mimura (2011) *GCA*, 75, 7063-7080. [3] L. Remusat et al. (2005) *GCA*, 69, 4377-4386.