

**CONVENTIONAL AND TMAH ASSISTED PYROLYSIS ON THE INSOLUBLE ORGANIC MATTER OF ORGUEIL AND MURCHISON.** L. Remusat<sup>1</sup>, S. Derenne<sup>1</sup> and F. Robert<sup>2</sup>, <sup>1</sup> Lab. de Chimie Bioorganique et Organique Physique, ENSCP, CNRS, Paris, FRANCE (laurent-remusat@enscp.jussieu.fr), <sup>2</sup> Lab. de Minéralogie, MNHN, CNRS, Paris, FRANCE.

**Introduction:** The organic matter (OM) in carbonaceous chondrites is distributed between a soluble fraction and a macromolecular one, insoluble in water and organic solvents, which accounts for almost 90 % of the OM. This insoluble organic matter (IOM) has been extensively studied through non degradative (such as NMR [1]) and degradative (e. g. pyrolysis [2]) techniques. All the data thus obtained point to an aromatic structure, cross-linked by short and branched aliphatic chains. However, in spite of a significant content in heteroatoms (respectively 16,5 % and 14,5 % of O and 2,8 % and 2 % N in Orgueil and Murchison IOM), very little is known about the polar moieties in the chondritic IOM. In contrast, numerous polar compounds (such as fatty acids, amino acids and polyols) have been identified in the soluble fraction of the meteorites. The identification of polar moieties in IOM should thus be a clue to answer the following question: is there a link between the soluble and the insoluble fractions in carbonaceous chondrites ?

Thanks to the addition of tetramethylammonium (TMAH) to samples prior to pyrolysis, polar moieties in refractory organic macromolecules can now be revealed [3]. This technique, which was first developed to investigate the chemical structure of lignins, also allowed recently to reveal the presence of proteinaceous moieties protected within the organic macromolecular network in Jurassic sedimentary rocks [4]. The present work thus aimed at determining the polar moieties in the IOM of the Orgueil and Murchison meteorites using pyrolysis with and without TMAH.

**Experimental:** In the present work, the IOM was isolated from the Orgueil and Murchison meteorites by the classical HF/HCl treatment followed by thorough extractions with a mixture of CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 2/1, v/v so as to remove any terrestrial contamination. IOMs were then submitted to Curie point pyrolysis with and without TMAH onto wires with a Curie temperature of 650°C. Two TMAH solutions were used for each meteoritic sample, differing from each other by the nature of the solvent, either MeOH or water. The pyrolysis device was directly coupled with a GC/MS system to analyse the effluents.

#### **Results and discussion:**

*Conventional pyrolysis:* In both meteorites, the pyrolysates are dominated by aromatic hydrocarbons ranging from benzene (one aromatic ring) to pyrene

(four aromatic rings). The abundance of the compounds decreases with the number of rings. The relative abundance of the main pyrolysis products was assessed after determination of their relative response factors upon GC/MS. C<sub>1</sub> to C<sub>4</sub>-alkylbenzenes and C<sub>1</sub> to C<sub>3</sub>-alkylnaphthalenes are identified and for each series of isomers, all the possible isomers are detected with similar abundances. This lack of isomeric selectivity was previously reported for soluble organic products in carbonaceous chondrites [5]. It is consistent with an organo-synthesis involving a random combination of precursors.

The main differences between the pyrolysis products released by the two meteorites concern the heteroatom-containing products. In agreement with a higher sulphur content in the meteorite, organo-sulphur compounds are more abundant upon pyrolysis of Murchison IOM than in that of Orgueil. In both cases, the organo-sulphur compounds are C<sub>1</sub> to C<sub>2</sub>-thiophenes, C<sub>0</sub> to C<sub>1</sub>-benzothiophenes and dibenzothiophene. These heterocycles may be produced upon pyrolysis by cyclisation of aliphatic chains linked by sulphur atoms but recent XANES studies revealed that at least a part of them is preexisting in the macromolecules [6]. Sulfur is also released as molecular sulfur in Murchison pyrolysate. Orgueil is characterized by a higher contribution of oxygen-containing compounds, namely C<sub>0</sub> to C<sub>2</sub>-phenols and aromatic ketones, than in Murchison, in agreement with its higher oxygen content. This higher contribution of oxygen-containing compounds reveals a higher oxidation state, as also observed upon S-XANES. This reflects either a more intense hydrothermal event or an oxidation occurring after the meteorite fall.

*Pyrolysis with TMAH:* Similar pyrochromatograms were obtained with TMAH in water and in MeOH on Orgueil IOM. Aromatic hydrocarbons are still abundant, with the same distribution than in conventional pyrolysis and no additional hydrocarbon was observed. Besides this, benzoic acid methyl esters, dimethoxy benzoic acid methyl esters, benzenedioic acid dimethyl esters and naphthalenoic acid methyl esters are now detected. These pyrolysis products reveal the occurrence of aromatic structures linked through ester bonds in the IOM. The latter are cleaved to release benzenecarboxylic acids which undergo

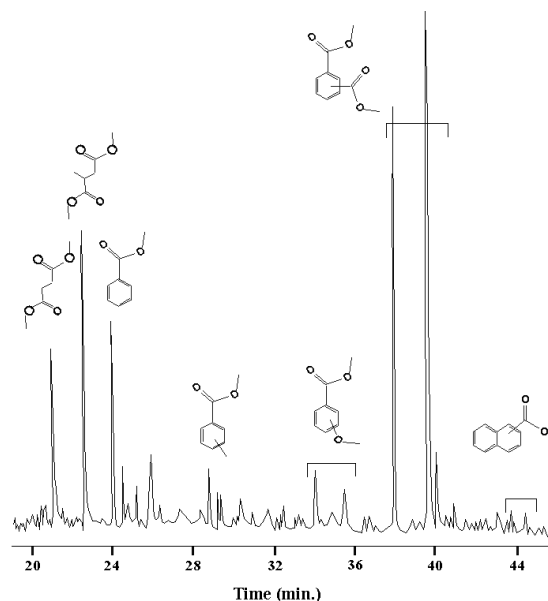
decarboxylations upon conventional pyrolysis, hence the only detection of the corresponding aromatic hydrocarbons. In contrast, in the present experiment, the acid function is preserved thanks to its methylation in the presence of TMAH (see fig. 1).

Benzene polycarboxylic acids and naphthalenoic acids were previously reported upon oxidative degradation of chondritic IOM [7], but they were derived from the oxidation of all the substituents of the aromatic moieties and were thus characterized by high number of acid functions per aromatic structure. Pyrolysis with TMAH thus allows to evidence the occurrence of ester linkages in the Orgueil IOM and the presence of benzenedioic acid methyl esters shows that some aromatic units are linked to the macromolecular network by two of these linkages. Another type of linkage is revealed by the occurrence of butanedioic acid dimethyl esters in the pyrolysate with TMAH.

It must be noted that no additional information on N- and S- containing could be derived from the pyrolysis with TMAH. Indeed, the only additional S-containing pyrolysis product identified after TMAH addition is the dimethylsulfone.

Pyrolysis with TMAH was also performed on Murchison IOM. The composition of the pyrolysate is being investigated and will be compared with that from Orgueil.

**Conclusion:** Our study using pyrolysis confirms the aromatic character of the IOM of Orgueil and Murchison. A detailed comparison between the pyrochromatograms from the 2 chondrites reveals minor differences: more thiophenes in Murchison, in agreement with a higher sulfur content, and more phenols and ketones in Orgueil, in agreement with a higher oxidation state of Orgueil. The TMAH thermochemolysis allowed us to reveal ester functions in Orgueil IOM. No additional information could be derived on N- and S- containing moieties. Further analysis will thus be required to test the occurrence of a link between the soluble and the insoluble OM in Orgueil and in Murchison.



**Figure 1:** Reconstructed ion chromatogram of the pyrolysate of Orgueil IOM in presence of TMAH showing acid methyl esters. We used  $m/z$  ion 59 (for butanedioic acid dimethyl esters), 135 (for methoxybenzoic acid methyl esters), 136 (for benzoic acid methyl ester), 150 (for methyl benzoic acid methyl esters), 163 (for benzenedioic acid dimethyl esters) and 186 (for naphthalenoic acid methyl esters). No relative abundance can be inferred from the above chromatogram.

#### References:

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