MOLECULAR AND ISOTOPIC CONSTRAINTS ON THE FORMATION OF THE INSOLUBLE ORGANIC MATTER OF CARBONACEOUS METEORITES

S. Derenne[1], F. Robert[2]

[1]CNRS/UPMC/EPHE, Paris, France, [2]MNHN/CNRS, Paris, France

Introduction

Carbonaceous meteorites are the most primitive objects of the solar system. They contain up to 4% of carbon, mainly occurring as insoluble organic matter (IOM). This IOM contains key information about the organo-synthesis processes taking place in the Solar system, which are so far poorly understood. The origin of the IOM of the carbonaceous meteorites remains an unsolved issue despite major achievements in the knowledge of its chemical structure. The latter led us to propose a model for its molecular structure, and to suggest that its formation took place in the gas phase of the disk surrounding the Sun in its early T-Tauri phase and that organic radicals played a central role in this organo-synthesis (Derenne and Robert, 2010).

To test experimentally this pathway, we submitted short hydrocarbons (methane, pentane, octane) to a microwave plasma discharge so as to produce *in situ* CH_x radicals. The black organic residue deposited contained both soluble and insoluble OM. The comparison at the molecular level between the synthesized IOM and that of meteorite led to strong similarities thus supporting the proposed pathway for its organo-synthesis (Biron et al., 2015).

However, isotopic variations in D and ^{15}N up to 2 orders of magnitude (in δ units) are observed in the IOM at three scales, bulk, sub-micron and molecular ones, likely reflecting variations in the physico-chemical conditions that prevailed in the gas. These variations are usually referred to as isotopic anomalies, indicating that they cannot be accounted for by the usual theory of isotope fractionation. Moreover, these preliminary experiments were focused on the hydrocarbon backbone of the IOM whereas the meteorite IOM is known to comprise heteroelements such as N (N/C of ca. 0.03), the origin of which remains unclear. To go a step further in the investigation of the potential formation of the meteorite IOM from organic radicals, on the one hand, we investigated the H and N isotope distributions in the synthesized IOMs and on the other hand, we performed syntheses with precursors comprising N or O.

Results

In the IOM synthesized from methane and octane, NanoSIMS analyses revealed large variations at a sub-micrometric spatial resolution (Robert et al., 2017). They likely reflect the differences in the D/H ratios of the CH_x radicals whose polymerization is at the origin of the IOM. These isotopic heterogeneities, usually referred to as cold and hot spots, are commensurable with those observed in meteorite IOM (Figure 1). As a consequence, the appearance of organic radicals in the ionized regions of the disk surrounding the Sun during its formation may have triggered the synthesis of organic compounds.

In the meteorite IOM, nitrogen mainly occurs within heterocycles along with a small contribution of nitrile groups, suggesting incorporation at the time of formation of the macromolecule. Syntheses were therefore performed to induce reactions between *in situ* produced CH_x radicals and N_2, NH_3 or NH_y radicals. Synthesized materials were thoroughly extracted to isolate IOM. The latter was then analyzed using the same methods as those previously used to decipher the chemical structure of the meteorite IOM, *i.e.* through a combination of spectroscopic methods (FTIR and solid state ^{13}C NMR) and pyrolysis coupled with GC-MS so as to achieve a comparison at the molecular level. All the syntheses led to the formation of IOM is formed and the latter showed some N incorporation (N/C between 0.02 and 0.08). N speciation (heterocycles and nitriles) is similar to that observed in meteorites. ^{15}N NanoSIMS analyses are in progress but preliminary results suggest that they allow distinguishing the IOMs produced with the different N sources, thus favoring some N incorporation pathway in the meteorite IOM.

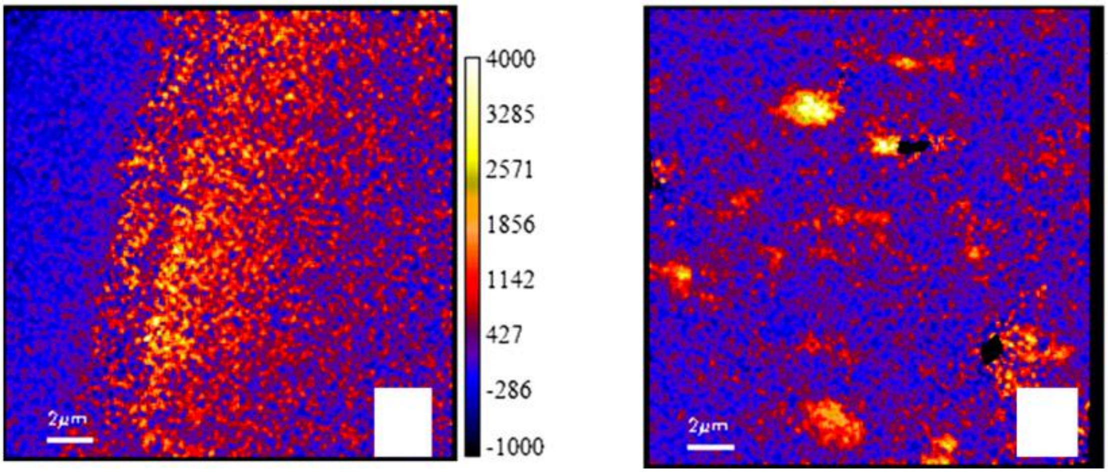

Figure 1 *NanoSIMS ion images of the D/H ratio in the IOM collected from (left) the methane plasma and (right) the Murchison meteorite. Both exhibits δD heterogeneities with rich areas termed hot spots.*

Conclusions

Organic plasmas were used to produce small radicals comprising C, H and N, which were involved in condensation reactions yielding IOM. The chemical structure of the synthesized IOM and the N speciation was compared with those of the meteorite IOM at the molecular level pointing to a major role of organic radicals in its formation. This is further supported by the isotope anomalies which could be reproduced for the first time in laboratory experiments. A strong production of organic radicals could have occurred at the surface of the disk surrounding the Sun during its formation, the latter being an intense UV source. This laboratory experiment thus shed a new light on the formation conditions and pathways of the IOM of carbonaceous meteorites and their incorporation of N.

References

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