
Introduction: This communication is concerned with the study of the chemical structure of the insoluble macromolecular organic matter (IOM) in carbonaceous meteorites. A better knowledge of this IOM in meteorites is essential to (i) estimate to what extent interstellar organic matter was preserved during the formation of the solar system and (ii) decipher the synthetic pathways of this matter in space. Although predominant (it accounts for 70 to 90 % of the total organic carbon of meteorites), the insoluble organic fraction has been much less extensively studied than the soluble one due to specific analytical difficulties. So far, the chemical structure of chondritic IOM has been mainly investigated through chemical and thermal degradation (e. g. Studier et al. [1]; Sephton et al. [2]) and only a limited number of spectroscopic studies have been performed on this type of material. Moreover, the latter were mainly performed in the 1970s-80s and considerable improvement of these tools has been achieved since then.

The present work reports the examination of the IOM of two carbonaceous meteorites, Orgueil and Murchison, through a number of various spectroscopic and microscopic methods, i.e. X-ray Absorption Near Edge Structure (XANES) for sulphur, carbon and nitrogen, solid state \(^{13}\text{C}\) Nuclear Magnetic Resonance (NMR), Electron Paramagnetic Resonance (EPR), Electron Nuclear Double Resonance (ENDOR) and High Resolution Transmission Electron Microscopy (HRTEM). To the best of our knowledge, this is the first time that such a wide range of methods is used for studying IOM in chondritic samples.

Results: The insoluble organic fraction was isolated via extensive aqueous and organic extractions followed by HF/HCl treatment and densimetric separation. The macromolecular IOM concentrates thus obtained are characterized by rather high carbon contents (67 and 50 % in Orgueil and Murchison, respectively) and relatively low amounts of residual minerals (9 and 22 %). The nature of these minerals was investigated using X-ray diffraction.

Sulphur K-edge XANES spectra led to the recognition of five different types of organic sulphur in Orgueil and Murchison and allowed to calculate their relative abundances. It also confirmed the strong contribution of pentlandite in Murchison minerals.

A high aromaticity was shown by the carbon and nitrogen K-edge XANES and solid state \(^{13}\text{C}\) NMR spectra. To get further insight into the nature and environment of carbons, a detailed \(^{13}\text{C}\) CP/MAS NMR study using variable contact times in the cross-polarization sequence and variable inversion delays in the inversion recovery cross-polarization sequence was carried out. It led to the recognition of 8 different types of carbon, the relative abundance of which could be calculated. This study revealed a high branching level in aliphatic chains, especially in Murchison, a much higher aromaticity fraction (ca. 0. 70) than previously considered (ca. 0.5; Cronin et al. [3]) and showed that most of these aromatic carbons are non-protonated. The typical pattern of the 2920-2960 cm\(^{-1}\) bands and the relative intensity of the 3050 cm\(^{-1}\) band in the FTIR spectra of Orgueil and Murchison IOMs (Ehrenfreund et al. [4]) are in agreement with the above NMR data. Moreover, a theoretical NMR-derived H/C atomic ratio could be calculated and compared to that derived from elemental analysis and revealed that a large part of the carbons are not detected by CP/MAS NMR (Gardinier et al. [5]). Two explanations can be put forward to account for this lack of detection: some carbons are too far from protons to be reached by magnetization transfer and/or spin/lattice relaxation times are reduced due to the occurrence of organic free radicals. The latter feature was recently considered by Cody et al. [6] in an NMR study of the IOM of Murchison.

The nature, distribution and abundance of the free radicals of the Murchison and Orgueil IOMs have therefore been investigated by multifrequency EPR at various temperatures and also by ENDOR spectroscopy. No EPR study had been performed on such material since the pioneer work of Duchesne et al. [7]. Radicals with a moderate level of oxygenation as indicated by their g-factor of 2.0031 were thus observed in the two samples. These radicals exhibit a relatively high average concentration (1.8 and 7.0 \(10^{18}\) g\(^{-1}\) for Murchison and Orgueil, respectively). Moreover, EPR saturation and ENDOR enhancement showed much higher local concentrations of radicals (about 3-4 \(10^{19}\) spin.g\(^{-1}\)). Such a local heterogeneity is, to the best of our knowledge, unique among natural organic macro-molecular materials and can thus be viewed as extraterrestrial signature. These radical-rich regions can be viewed as pristine parts of the OM which would have survived the hydrothermal process on the parent body.

All the above analyses along with previous pyrolysis and chemical degradation data indicate a highly aromatic character for these materials. How-
ever, no clear-cut information was obtained on the size of the polyaromatic units. Indeed, two types of units can be considered to account for the spectroscopic and pyrolytic data, either large polyaromatic units or smaller, but highly substituted, ones. HRTEM in the lattice fringe mode was coupled with an original lab-made quantitative analysis of the images developed to characterize the structure of poorly organised carbons (Reynaud et al [8]). This new approach was thus used to assess the average size and the extent of organization of these units in Orgueil and Murchison IOMs. It revealed a poor structural organization (Fig. 1). The units comprise relatively subnanometric layers with an average size of 3-4 rings in diameter. Moreover, a rather high amount of single layers (ca.50 %) is noted whereas stacks are only made of a few layers, with an average of about 2.4 layers/stack. This is clearly in favour of the occurrence of small, highly substituted, aromatic units rather than large polyaromatic ones in the IOM of the two meteorites. Accordingly, the IOM in these meteorites did not undergo a marked thermal maturation upon the hydrothermal process on the parent body. A model of synthesis, involving a statistical combination of all possible bonds between CH3, CH2 and CH radicals can thus be proposed for both the aliphatic and aromatic moieties of this OM.

**Conclusion**: A combination of various complementary spectroscopic and microscopic tools appears as a powerful analytical approach in the elucidation of the chemical structure and origin of the insoluble organic fraction of meteorites, as also observed for other complex organic macromolecular materials (Derenne et al. [9]; Poirier et al. [10]). EPR data points to the preservation of pristine areas in the OM fraction not affected by subsequent hydrothermal events. Taken together, the obtained results led to propose a model for the chemical structure of the insoluble organic matter of the Orgueil and Murchison meteorites and hence for organosynthesis in space. This model could explain not only the chemical features of the insoluble organic matter in meteorites but also the typical FTIR signature of the interstellar medium. Therefore, organic material found in the interstellar medium and that incorporated in the most primitive objects of the solar system probably share a common organosynthesis.


![FIG. 1: HRTEM of the IOM of the Orgueil meteorite](image)