3.2.14

Characterization of the aromatic units of the insoluble organic matter from carbonaceous chondrites

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The primitive carbonaceous chondrites contain substantial amounts of carbon (up to 3%), mostly occurring in macromolecular insoluble organic matter (IOM). This IOM is considered as a record of interstellar synthesis and may contain precursors of prebiotic molecules possibly deposited on earth by meteoritic bombardments. For these reasons, chondritic IOM has been raising interest for long and it is now well established that the chemical structure of this macromolecular material is based on aromatic moieties linked by short aliphatic chains and comprising substantial amounts of heteroatoms. However, due to limitations on analytical tools, its precise chemical structure and especially the abundance and size of the aromatic moieties are still a matter of debate.

To characterize the aromatic units in chondritic IOM is important to determine the conditions involved in space in their synthesis. Indeed, likely due to their high stability, polyaromatic structures are among the most abundant and widespread organic structures in the universe and may represent a link between the interstellar medium and the solar system. In the present work, we used two non-destructive techniques, namely solid state ^{13}C nuclear magnetic resonance (NMR) and high resolution transmission electron microscopy (HRTEM) to determine the abundance and the main features of the aromatic units in the IOMs isolated from three carbonaceous chondrites, Orgueil, Murchison and Tagish Lake using the classical HF/HCl treatment.

The combination of these two techniques allows a precise comparison between the three meteorites. Above all, it reveals that the aromatics that build up the macromolecular network of the meteoritic IOM are of rather small size and highly substituted (i.e. they are characterized by a low content in peripheral hydrogens). These features are especially marked for Murchison.

When compared to that reported for polyaromatics in the interstellar medium, the size of the aromatic moieties in the meteoritic IOM is significantly lower. Such a difference may reflect different organosynthetic pathways for aromatic moieties in the two environments However, a common origin cannot be excluded, the smallest aromatic units being preferentially preserved against photodissociation in the chondritic OM.

3.2.15

In situ polymerisation of labile lipids as a source for the aliphatic component of recalcitrant macromolecules in sedimentary materials

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Kerogen formation, has been attributed either to selective preservation of resistant biomacromolecules or to random polymerisation of labile biomolecules, i.e. neogenesis. To evaluate these divergent models, we investigated fossil leaves from the Ardèche diatomite (Late Miocene, southeast France) using chemical and morphological techniques and compared them to their modern equivalents.

The fossil leaves, characterised by selective chemical degradation , py-GC-MS, FTIR and solid state ^{13}C NMR consist predominantly of a recalcitrant (non hydrolysable) largely aliphatic geopolymer. TMAH-assisted pyrolysis revealed the aliphatic polymer to consists of fatty acyl subunits ranging from C_8 to C_{32} with a predominance of the C_{16} and C_{18} units. TEM and SEM investigations of the fossils reveal no evidence for cuticle preservation.

Analysis of modern plants reveal that cutan as defined as a non hydrolysable polymer is present only in 3 out of 23 plants analysed. It is absent in modern equivalents of all of the Ardèche diatomite leaves, hence cutan cannot be a source for the aliphatic macromolecule in the fossil leaves, precluding selective preservation.

However, C_{16} and C_{18} fatty acyl units are predominant in the cutin and phospholipid fatty acid (PLFA) fraction, while C_{10} to C_{32} acid units are characteristic of the free fatty acid (FA) fraction of epicuticular waxes. Thus the aliphatic macromolecule in the fossil leaves could be derived from the *in situ polymerisation* of labile cell membrane lipids and free fatty acids.

To further confirm that labile lipid components can be a source of geological macromolecules, artificial maturation experiments using gold tube confined pyrolysis (350 °C 700 Bars) were conducted on modern leaves, shrimp, cockroach and scorpion. The untreated samples successfully generated an aliphatic polymer similar to that in the fossils whereas lipid extracted samples failed to do so; this provides direct experimental evidence for labile lipids as a source for the aliphatic macromolecule.