

POLYCYCLIC AROMATIC HYDROCARBONS IN CARBONACEOUS CHONDRITES. M. Lecasble¹, L. Remusat¹, J.-C. Viennet¹, B. Laurent¹, S. Bernard¹, ¹Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie, Sorbonne Universités, CNRS UMR 7590, Muséum National d'Histoire Naturelle, Paris. E-mail : marceau.lecasble@mnhn.fr.

Introduction: Organic matter in carbonaceous chondrites (CC) occurs as an aromatic-rich macromolecule called insoluble organic matter (IOM) and a diverse suite of soluble compounds including polycyclic aromatic hydrocarbons (PAHs) consisting of two or more fused benzene rings [1]. These compounds have also been detected in abundance in the interstellar medium (ISM) [2], galaxies [3] and around stars [4]. They have been proposed to constitute one of the main carbon carrier form.

The ubiquitous nature of PAHs potentially makes them good tracers of accretion processes. But after their accretion in the protoplanetary disk, all chondrite parent bodies were affected by secondary processes due to the radioactive decay of short-lived radionuclides, mainly ²⁶Al. Among these processes, aqueous alteration [5] may have modified the accreted PAHs [6], both chemically and isotopically.

Here, we characterized PAHs from four recent falls having experienced different degree of aqueous alteration : three CM chondrites from the asteroid belt, namely Kolang (CM1/2, [7]), Mukundpura (CM2.0, [8]) and Aguas Zarcas (CM2.2, [9]), and a C2 ungrouped chondrite resembling Tagish Lake, namely Tarda [10], possibly being a fragment of a D-type asteroid [11].

Methods: PAHs were isolated using a Dionex™ Accelerated Solvent Extractor, identified by GC-MS and quantified by GC-FID. Carbon and hydrogen isotope ratios of the most abundant have been measured using GC-irMS when possible.

Results: We observed strong differences in the PAH content of the meteorite investigated, with concentrations in Tarda (2 ppm) lower than in Kolang (20 ppm), in Aguas Zarcas (23 ppm) and in Mukundpura (31 ppm). The PAH contents of the CM investigated here fell in the range of those reported for the two famous CM Murchison [12] and Paris [13]. The total PAH content of Tarda was similar to that of Tagish Lake [14].

Up to 79 different PAHs (Fig. 1) were detected, with sizes ranging from 2 to 5 cycles (naphthalene to benzopyrene/perylene). Of note, only 14 PAHs were quantified in Tarda (concentration > 0.03 ppm). Most abundant PAHs in the CM investigated were fluoranthene and pyrene (m/z 202), as previously reported

[12,13,15], while it was naphthalene (m/z 128) in Tarda. Naphthalene/phenanthrene and phenanthrene/pyrene decrease in the order TA > MK > AZ > KO.

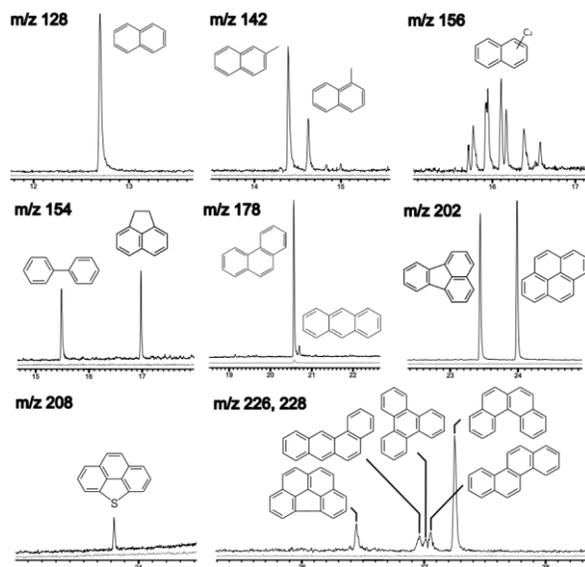


Fig 1. Some Kolang GC-MS selective ion chromatograms. Most abundant PAHs are fluoranthene and pyrene (m/z 202) followed by phenanthrene (m/z 178) and naphthalene (m/z 128). Naphthalene alkylation serie corresponds to m/z 128, 142 (C1-Na : 2MN and 1MN), 156 (C2-Na) and 170 (C3-Na, not shown).

Heteroatom (NSO) containing PAHs were also detected. Among them were heterocycles (S and N), ketones and ether (O) containing PAHs. We also detected, for the first time, benzothiophenes, benzophenones and phenanthrothiophenes. Also, alkylated products of naphthalene (Fig. 2), biphenyl, phenanthrene, anthracene, fluoranthene and pyrene were present with up to three additional carbons and concentrations increasing in the order TA < AZ < MK < KO. At last, we determined the methyl naphthalene ratio (MNR = 2MN/1MN), an indicator of thermal maturity for IOM. Tarda exhibited the lowest MNR, while it increased from Mukundpura to Kolang with Aguas Zarcas displaying intermediate values.

The carbon isotope composition ($\delta^{13}\text{C}_{\text{PDB}}$) of the measured PAHs ranged from -15 to 2‰. Furthermore, the hydrogen isotope composition of two PAHs could be measured for the three CM investigated (Fig. 3),

leading to δD_{VSMOW} values ranging from -263‰ to -153‰.

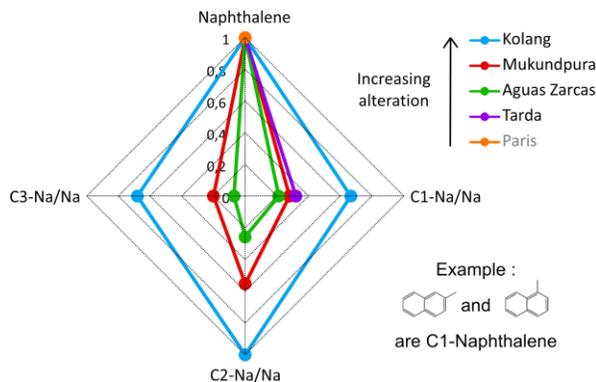


Fig 2. Spider graph representing naphthalene alkylation serie in Kolang, Mukundpura, Aguas Zarcas, Tarda and Paris [13]. For each point, concentrations of alkylated isomers are summed up and normalized to the naphthalene one. Kolang contains the most of alkylated products.

Discussion: The concentration of PAHs is not correlated to the degree of alteration of CMs. Also, PAH carbon isotope ratios show a ^{13}C -depletion with increasing carbon number, consistent with two reaction pathways (pyrene and fluoranthene series), as described by [15], suggesting a PAH synthesis through cyclization in the interstellar medium.

Yet, the extent of alkylation of CMs, increasing in the order $\text{PA} < \text{AZ} < \text{MK} < \text{KO}$ seems correlated to the degree of alteration (Fig. 2) [16]. Heteroatom containing PAHs are affected in different ways and MNR surprisingly increases, whereas this ratio decreases in IOM pyrolysates.

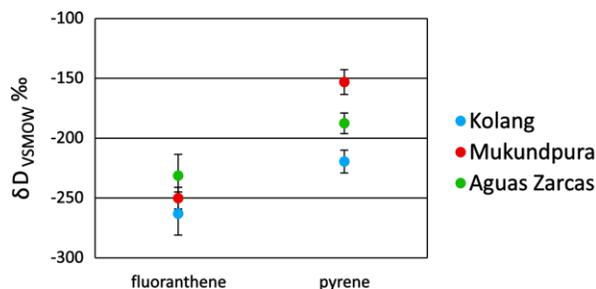


Fig 3. Fluoranthene and pyrene hydrogen isotope ratio (in δD_{VSMOW} ‰) in Kolang, Mukundpura and Aguas Zarcas. Values are here deuterium-depleted compared to IOM, possibly because of hydrogen isotope exchange with D-poor water during alteration.

Finally, while extraterrestrial OM is usually deuterium-enriched as a result of the low-temperature chemistry in the ISM [17] or in the protosolar nebula [18], the PAHs of the CM investigated are deuterium-depleted (Fig. 3). This depletion may indicate hydrogen exchange with D-poor water during (secondary) aqueous alteration processes having taken place on the parent body. Indeed, water in Mukundpura ($\delta D = -422$ ‰) and Aguas Zarcas ($\delta D = -377$ ‰) [19] exhibits low values.

Conclusions: PAHs were likely synthesized in the ISM, having their carbon signature undisturbed by secondary processes on the parent body. However, they recorded aqueous alteration in chondrite parent bodies through a multifaceted molecular evolution and the loss of their hydrogen isotope signature.

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