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Polycyclic aromatic hydrocarbons in carbonaceous chondrites can be used as tracers of both pre-accretion and secondary processes



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ABSTRACT

Carbonaceous chondrites contain a diverse suite of more or less soluble compounds, including polycyclic aromatic hydrocarbons (PAHs). These compounds are structured around two or more fused benzene rings, and have shown to be detected in various astrophysical environments. The origin of PAHs in carbonaceous chondrites is debated: they may originate from the interstellar medium (ISM) and thus potentially carry information on accretion processes. Alternatively, they may have formed or transformed during secondary processes on parent bodies and thus carry information about aqueous alteration conditions. Here, we investigate the nature, quantity, and isotopic composition of free PAHs in three recently recovered CM chondrites having experienced substantial and distinct degrees of alteration: the CM2.2 Aguas Zarcas, the CM2.0 Mukundpura and the CM1/2 Kolang. All the CMs investigated contain PAHs, with sizes ranging from 2 (naphthalene) to 5 cycles (benzopyrene). The concentration of PAHs is not correlated to the degree of alteration and larger PAHs are also the most depleted in ^{13}C , suggesting an interstellar origin. Yet, the abundance of alkylated PAHs appears correlated to the degree of alteration and all the extracted PAHs are D-depleted, pointing towards hydrogen exchange with water having occurred during aqueous alteration. These combined results suggest that PAHs in CCs likely carry information on both accretion and alteration processes.

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1. Introduction

Carbonaceous chondrites (CC) are fragments of asteroids which accreted interstellar materials and ice/dust processed in the protoplanetary disk, including diverse organic compounds (Cronin et al., 1988; Scott and Krot, 2003; Ehrenfreund et al., 2005; Weisberg et al., 2006; Remusat et al., 2006, 2009, 2016; Herbst and Dishoeck, 2009; Aléon, 2010; Boogert et al., 2015). Some of these organic compounds may have been produced before accretion via a number of interstellar and nebular processes, such as plasma-induced condensation reactions occurring at elevated temperatures (up to 1000 K) (Sagan and Khare, 1979; Saito and Kimura, 2009; Kuga et al., 2015), gas-grain reactions occurring at moderate temperatures (<600 K) (Anders et al., 1973; Llorca and Casanova, 2000; Nuth et al., 2008) or irradiation-driven and temperature-driven reactions occurring within ices at low temperature (<280 K) (Muñoz Caro and Schutte, 2003; Ciesla and Sandford, 2012; Theulé et al., 2013; Vinogradoff et al., 2013; Laurent et al., 2015).

Following the accretion, asteroids have all experienced secondary processes, including aqueous alteration episodes triggered by the melting of ice due to the radioactive decay of short-lived radionuclides such as ^{26}Al (McSween, 1979; Brearley, 2006; Krot et al., 2006; Verdier-Paoletti et al., 2017; Fujiya, 2018; Suttle et al., 2021). These episodes produced secondary mineral phases, mainly smectite and/or serpentine phyllosilicates, carbonates and/or sulfides (Brearley, 2006; Le Guillou and Brearley, 2014; Le Guillou et al., 2014; Yesiltas and Kebukawa, 2016; Nittler et al., 2019; Vollmer et al., 2020) and modified the organic compounds initially present in various ways while forming a diversity of new ones (Cody et al., 2011; Le Guillou et al., 2014; Kebukawa and Cody, 2015; Vinogradoff et al., 2017, 2018; Changela et al., 2018; Viennet et al., 2022).

Overall, CCs contain up to 5 wt% of organic matter dominated by an insoluble fraction (IOM - 75 to 90 wt%) associated with a minor soluble fraction (SOM - 10 to 25 wt%). While the IOM consists in high molecular weight molecules made of aromatic units and short aliphatic chains rich in hetero-elements (Cody and Alexander, 2005; Alexander et al., 2007; Derenne and Robert, 2010; Remusat et al., 2016, 2019; Vinogradoff et al., 2017; Danger et al., 2020), the SOM is composed of a diversity of small organic molecules

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(such as carboxylic acids, amino acids, nucleobases, sugars... - e.g., Pizzarello, 2006; Remusat, 2015; Martins et al., 2015) including polycyclic aromatic hydrocarbons (PAHs) (Oró et al., 1971; Pering and Ponnampuruma, 1971; Basile et al., 1984; Zenobi et al., 1989; Gilmour and Pillinger, 1994; Messenger et al., 1998; Sephton et al., 1998; Naraoka et al., 2000; Oba and Naraoka, 2003; Plows et al., 2003; Huang et al., 2015; Simkus et al., 2019; Kalpana et al., 2021).

Poorly soluble, PAHs are organic molecules consisting of two or more fused benzene rings (Richter and Howard, 2000; Abdel-Shafy and Mansour, 2016). It has been suggested that asteroids accreted PAHs having formed in the interstellar medium (ISM) (Yang and Epstein 1983, 1984; Kerridge, 1983; Allamandola et al., 1987; Plows et al., 2003). In fact, PAHs are abundant in the ISM, comprising up to 20% of its carbon material (Leger and Puget, 1984; Allamandola et al., 1985, 1989). Plus, in CCs, the carbon isotopic composition of PAHs is consistent with a formation through cyclization/carbon addition at low temperatures, potentially in the ISM (Gilmour and Pillinger, 1994; Naraoka et al., 2000). Yet, the PAHs of the ISM display sizes ranging from 50 to 100 carbon atoms (Tielens 2008, 2011), in contrast with those of the PAHs found in CCs which range from 10 (naphthalene) to 24 carbon atoms (coronene) (Gilmour and Pillinger, 1994; Becker and Bunch, 1997; Naraoka et al., 2000; Sephton, 2002). Also, while small PAHs experience alkylation or melting under aqueous alteration processes (Elsila et al., 2005; Giese et al., 2019), the relatively big PAHs seem to withstand simulated asteroidal conditions (Giese et al., 2019). The hydrogen isotope composition could help with confirming this accretion scenario since the PAHs of the ISM are expected to be D-rich (Allamandola et al., 1989; Tielens, 1997; Millar et al., 2000; Peeters et al., 2004). However, only two studies have discussed the hydrogen isotopic compositions of PAHs so far (Oba and Naraoka, 2003; Huang et al., 2015) and their results are not consistent with each other. It still remains unclear at this stage if PAHs of CCs may provide information on accretion processes, alteration processes, both, or none.

Here we investigate the nature, concentration and carbon and hydrogen isotopic compositions of the free PAHs extracted from three CM chondrites having experienced substantial and distinct degrees of aqueous alteration: Kolang (CM1/2), Mukundpura (CM2.0) and Aguas Zarcas (CM2.2). We discuss here the possible origin of these PAHs. Because the chondrites investigated here belong to the CM class, it can be assumed that they are fragments of the same parent body (or of identical parent bodies that accreted the same mixture of precursors). Their comparison thus also allows discussing the potential impact of secondary alteration processes on PAHs of CCs.

2. Materials and methods

2.1. Carbonaceous chondrites

Kolang (CM1/2), Mukundpura (CM2.0) and Aguas Zarcas (CM2.2) chondrites were all provided by Labenne meteorites. They are all recent falls and were thus submitted to only very little terrestrial alteration/contamination. Kolang (KO) is a breccia containing CM1 clasts (Schrader et al., 2021) which fell in Indonesia in 2020 and was classified as a CM1/2 based on its mineralogy and oxygen isotopic composition (Gattacceca et al., 2021). Mukundpura (MK) is an unbrecciated chondrite which fell in India in 2017 and was classified as a CM2.0 (Tripathi et al., 2018; Rudraswami et al., 2019). Aguas Zarcas (AZ) is a very heterogeneous breccia showing different lithologies which fell in Costa Rica in 2019 (Lücke et al., 2019) and classified as a CM2.2 (Kerraouch et al., 2021). The water-soluble compounds of the CM samples

were previously extracted in pure water at 100 °C as reported in Serra et al. (2022). Thanks to the water insolubility of PAHs (Mackay and Shiu, 1977), this step did not modify the nature, concentration and carbon and hydrogen isotopic compositions of the free PAHs (e.g. no naphthalene was detected in the water extracts - Oba and Naraoka, 2003).

2.2. PAH extraction

About 2 g of each meteorite were extracted using a Dionex™ Accelerated Solvent Extractor ASE™ 150 (Thermo Scientific™). Dichloromethane/methanol mixture (DCM/MeOH - 9:1) was used as solvent. Following regular protocols (Wang et al., 2007; Quéneá et al., 2012; El-Mufleh et al., 2014; Cennerazzo, 2017), each run of extraction consisting in 3 cycles of 5 min at 80 °C for 1 g of meteorite. Between each run, the ASE was rinsed 5 times at 150 °C and all of the extractor parts were cleaned in an ultrasonic bath of solvent for 10 min. Two runs were combined for each meteorite. A blank was produced using a diatomite heated beforehand at 1000 °C. About 14 mL of PAH-rich solvent were collected for each meteorite, and evaporated down to 2 mL under N₂ stream (>99.999%; Air Liquide, ALPHAGAZ 1). It is a possibility that small PAHs were lost during the extraction of water-soluble compounds or during the N₂ stream reduction (Basile et al., 1984; Krishnamurthy et al., 1992; Martins et al., 2015; Kalpana et al., 2021). Yet, small PAHs such as naphthalene, were detected, making the present protocol as efficient as supercritical fluid extraction (SFE) procedures (Sephton et al., 1998; Wicker et al., 2018; Librando et al., 2004).

2.3. Gas Chromatography-Mass Spectrometry analyses

The PAHs were identified using a ThermoScientific 1310 GC coupled with an ISQ7000 MS operating at METIS (Paris, France). The GC was equipped with a RTX-5Si/MS (60 m × 0.25 mm, 0.25 µm film) capillary column, suitable for hydrocarbons. Ultra-high-quality helium was used as carrier gas. The samples were injected with a TriPluRSH autosampler, in split mode with a ratio of 13:2 and the injector temperature was set at 280 °C. After 3 min at 60 °C, the temperature was increased along a ramp of 10 °C/minute up to 290 °C to be held 15 min. Solvent delay was set at 3 min. Measurements were performed using an ion source temperature of 300 °C, an electron energy of 45 eV and a scanning rate of 5 scan/s from 35 to 700 *m/z* with a mass selective detector (conversion dynode with electron multiplier). Interface temperature was set at 300 °C. The OpenChrome software was used for data processing, including background noise removal. Compounds were identified using the NIST database in selective ion MS mode.

2.4. Gas Chromatography-Flame Ionization Detector analyses

The PAH quantification was performed via Agilent Technologies 7890B GC coupled with a flame ionization detector (FID) operated at IMPMC, MNHN (Paris, France). The GC was equipped with a HP-5 (30 m × 0.32 mm, 0.25 µm film) capillary column coated with (5%-Phenyl)-methylpolysiloxane. Ultra-high-quality helium was used as carrier gas. The samples were injected in split mode with a ratio of 2 and the injector temperature was set at 280 °C. After 3 min at 60 °C, the temperature was increased along a ramp of 10 °C/minute up to 290 °C to be held 15 min. A standard solution of three PAHs (naphthalene, phenanthrene and pyrene - Sigma Aldrich) was used for quantification with a 10–20% estimated uncertainty. The quantification limit was set at 0.03 ppm.

2.5. Gas Chromatography-isotope ratio Mass Spectrometry analyses

Compound-specific carbon and hydrogen isotope analyses were performed on an Elementar VisION isotopic mass spectrometer interfaced with an Agilent Technologies 7890B GC through a GC5 Furnace system, at IMPMC, MNHN (Paris, France). Ultra-high purity helium was used as carrier gas. The oven was fitted with a HP-5 fused silica column (30 m × 0.32 mm, 0.25 μm film). Five μL of each extract were injected at 280 °C in split mode with a ratio of 2. After 1 min at 80 °C, the temperature was increased along a ramp of 1 °C/minute up to 250 °C to be held 1 min. Solvent delay was set at 8 min. The injection of the samples into the Elementar GC5 Furnace System produced either CO₂ thanks to a quartz tube at 950 °C with CuO/Pt as oxidizer or H₂ thanks to a ceramic tube at 1250 °C. The CO₂ or H₂ isotopic ratios were measured using the irMS for each molecule. Each sample was analysed five times. The hydrogen isotopic composition of only the two most abundant PAHs could be measured. Results were corrected using international standards (naphthalene and phenanthrene, Indiana University). A session drift correction has been applied using in-house standards (phenanthrene and pyrene, Sigma Aldrich). An additional H₃⁺ correction was calculated and applied for the determination of hydrogen isotopic compositions. Carbon isotopic ratios are expressed in the δ notation relative to the international Pee Dee Belemnite standard following the equation:

$$\delta^{13}\text{C}_{\text{PDB}} \text{‰} = \left[\left(\frac{^{13}\text{C}}{^{12}\text{C}} \right)_{\text{sample}} / \left(\frac{^{13}\text{C}}{^{12}\text{C}} \right)_{\text{PDB}} - 1 \right] * 10^3.$$

Hydrogen isotopic ratios are expressed in the δ notation relative to the Vienna Standard Mean Ocean Water following the equation:

$$\delta\text{D}_{\text{VSMOW}} \text{‰} = \left[\left(\frac{\text{D}}{\text{H}} \right)_{\text{sample}} / \left(\frac{\text{D}}{\text{H}} \right)_{\text{VSMOW}} - 1 \right] * 10^3.$$

3. Results

3.1. PAH absolute concentrations and relative abundances

The CMs investigated contain PAHs as revealed by GC–MS chromatograms (Fig. 1). The total concentration of PAHs in the CMs reaches 24.6 ppm for Aguas Zarcas, 34.4 ppm for Mukundpura and 22.0 ppm for Kolang (Table 1 and Fig. 2). These values are comparable to those reported for Murchison (21.6 ppm - Pering and Ponnamperuma 1971) and slightly higher than those reported for Paris (8.7 ppm - Martins et al., 2015). Of note, the measured concentration of PAHs in Mukundpura is much lower than 505 ppm reported by Kalpana et al. (2021). The CMs investigated here dis-

play a diversity of PAHs, and the selective ion chromatograms of PAHs from Kolang are shown on Fig. 3. In total, 25 different *m/z* were detected in all CMs, corresponding to more than 75 different PAHs (Table 1), ranging in size from naphthalene (2 cycles - 10 carbon atoms) to benzopyrene and perylene (5 cycles - 20 carbon atoms). In good agreement with results obtained on other CCs (Commins and Harington, 1966; Basile et al., 1984; Krishnamurthy et al., 1992; Pering and Ponnamperuma, 1971; Naraoka et al., 2000; Elsila et al., 2005; Huang et al., 2015; Martins et al., 2015; Kalpana et al., 2021), the most abundant PAHs here are pyrene (12–22%; 4.8–5.6 ppm), fluoranthene (15–22%; 4.1–5.6 ppm) and phenanthrene (11–13%; 2.4–3.9 ppm) (Table 1).

3.2. Hetero-PAHs

A number of hetero-PAHs were detected in the CMs investigated (Table 1), among which were S-containing PAHs (benzothiophene, dibenzothiophene and phenanthro[4,5-*bcd*]thiophene), O-containing PAHs (benzophenone, 9H-fluoren-9-one and 1-(phenylmethoxy)-naphthalene) and a N-containing PAH (carbazole). Note that in Kolang, no benzophenone was detected and the 1-(phenylmethoxy)-naphthalene could not be quantified. In any case, this is the first report of benzothiophene, benzophenone and phenanthrothiophene in CCs. The content of O-PAHs of Kolang is lower to that of Mukundpura and Aguas Zarcas (1.9% vs 6% of total PAHs), while the contents of N- and S-PAHs are similar for these three CMs (1 and 5%). These values are roughly similar to those previously reported for Murchison (Basile et al., 1984) and Mukundpura (Kalpana et al., 2021). Hexathiane (S₆) was found in the 3 CMs, confirming previous reports for Aguas Zarcas (Tunney et al., 2022).

3.3. Alkylated PAHs

Alkylated PAHs are PAHs having hydrocarbon functional groups substituted onto the parent structure. These substituents can range from one hydrocarbon group, known as C1-PAHs, to much larger hydrocarbon groups. In the CMs investigated here, we detected series of alkylated PAHs up to C3-naphthalene, C3-phenanthrene, C2-pyrene, C1-phenylbenzene, C1-anthracene and C1-fluoranthene (Table 2). The naphthalene and phenanthrene series reveal that alkylation is more pronounced for the CM1/2 Kolang than for the CM2s Aguas Zarcas and Mukundpura (Figs. 2 and 4).

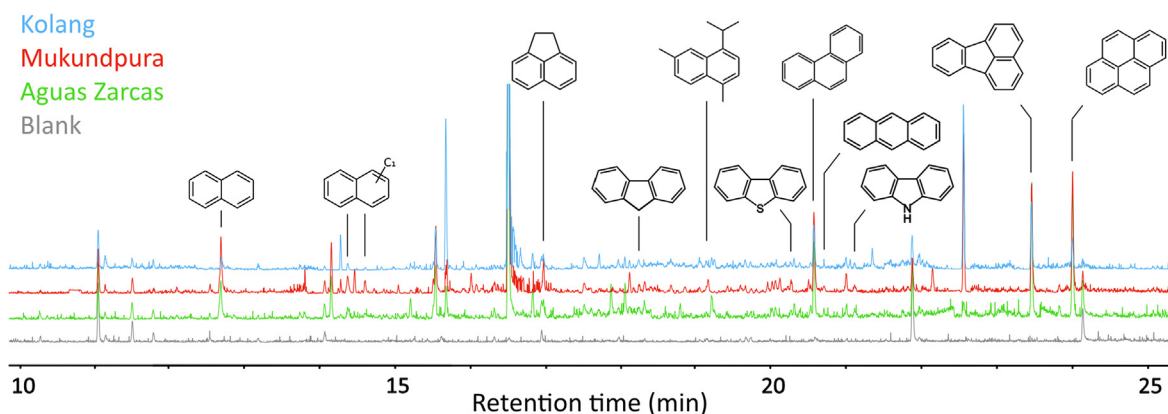


Fig. 1. GC–MS chromatograms of DCM/MeOH extracts of the Kolang, Mukundpura, Aguas Zarcas meteorites. Blank chromatogram and some PAHs are shown. More abundant PAHs are naphthalene (2 aromatic rings), phenanthrene (3), fluoranthene and pyrene (4). Peaks of other compounds (listed in Appendix A) either correspond to contaminants from solvents and glassware, also detected in the blank, or due to the presence in the extracts of other molecular families, such as alkanes and benzene containing hydrocarbons.

Table 1

PAH concentrations in Kolang, Mukundpura and Aguas Zarcas. PAHs have been identified using GC–MS and quantified using GC-FID. n.q. = not quantified (<0.03 ppm), n.d. = not detected.

Retention Time (minutes)	Aromatic Hydrocarbon	Molecular ion (<i>m/z</i>)	Formula	Concentration (ppm)		
				Kolang	Mukundpura	Aguas Zarcas
12.70	Naphthalene	128	C10H8	0.91	3.55	1.84
12.84	Benzothiophene	134	C8H6S	0.03	0.12	0.06
14.38	2-methylnaphthalene	142	C11H10	0.42	0.63	0.26
14.61	1-methylnaphthalene	142	C11H10	0.18	0.37	0.13
15.52	Biphenyl	154	C12H10	0.73	1.30	0.86
15.68	C2-Naphthalene	156	C12H12	0.03	n.q.	n.d.
15.74	C2-Naphthalene	156	C12H12	0.08	0.12	0.05
15.77	C2-Naphthalene	156	C12H12	0.05	0.08	0.03
15.90	C2-Naphthalene	156	C12H12	0.12	0.10	0.05
15.93	C2-Naphthalene	156	C12H12	0.15	0.13	0.06
16.09	C2-Naphthalene	156	C12H12	0.18	0.26	0.08
16.16	C2-Naphthalene	156	C12H12	0.12	0.16	0.05
16.18	Naphthalene, 1-(2-propenyl)-	168	C13H12	0.04	0.08	0.04
16.37	C2-Naphthalene	156	C12H12	0.08	0.13	0.06
16.40	C2-Naphthalene	156	C12H12	0.04	0.07	0.03
16.58	C2-Naphthalene	156	C12H12	0.06	0.91	0.04
16.89	Diphenylmethane	168	C13H12	0.15	0.21	0.12
16.98	Acenaphthene	154	C12H10	0.91	1.83	0.69
17.18	C3-Naphthalene	170	C13H14	0.05	0.05	n.q.
17.21	C3-Naphthalene	170	C13H14	0.03	0.04	n.q.
17.28	C3-Naphthalene	170	C13H14	0.04	0.05	n.q.
17.42	C3-Naphthalene	170	C13H14	0.08	0.08	0.03
17.52	C3-Naphthalene	170	C13H14	0.08	0.09	0.03
17.71	C3-Naphthalene	170	C13H14	0.07	0.08	0.03
17.77	C3-Naphthalene	170	C13H14	0.08	0.08	0.03
17.92	C3-Naphthalene	170	C13H14	0.05	0.07	n.q.
17.96	C3-Naphthalene	170	C13H14	0.04	0.05	n.q.
18.13	C3-Naphthalene	170	C13H14	0.04	0.05	n.q.
18.24	Fluorene	166	C13H10	0.61	0.45	0.30
18.24	C3-Naphthalene	170	C13H14	0.03	0.05	n.q.
18.37	1-Isopropenylnaphthalene	168	C13H12	0.15	0.21	0.09
18.40	Benzene, [1-(2,4-Cyclopentadien-1-ylidene)ethyl]-	168	C13H12	0.19	0.31	0.13
18.45	C1-Biphenyl	168	C13H12	0.16	0.23	0.11
18.45	C3-Naphthalene	170	C13H14	0.03	0.04	n.q.
18.52	C1-Biphenyl	168	C13H12	0.11	0.13	0.06
18.56	C1-Biphenyl	168	C13H12	0.22	0.23	0.13
18.66	Benzophenone	182	C13H10O	n.q.	0.90	0.46
19.16	Cadalene	198	C15H18	n.d.	0.41	n.d.
20.06	9H-Fluoren-9-one	180	C13H8O	0.41	0.99	0.73
20.26	Dibenzothiophene	184	C12H8S	0.33	0.52	0.39
20.56	Phenanthrene	178	C14H10	2.36	3.91	3.02
20.70	Anthracene	178	C14H10	0.18	0.29	0.29
21.11	Carbazole	167	C12H9N	0.22	0.33	0.27
21.75	C1-Phenanthrene	192	C15H12	0.17	0.18	0.17
21.81	C1-Phenanthrene	192	C15H12	0.16	0.16	0.14
21.93	C1-Anthracene	192	C15H12	0.05	0.05	0.04
22.00	C1-Phenanthrene	192	C15H12	0.20	0.18	0.16
22.06	C1-Phenanthrene	192	C15H12	0.12	0.12	0.12
22.83	C2-Phenanthrene	206	C16H14	0.05	n.q.	0.04
22.92	C2-Phenanthrene	206	C16H14	0.05	n.q.	0.04
23.09	C2-Phenanthrene	206	C16H14	0.12	0.09	0.11
23.16	C2-Phenanthrene	206	C16H14	0.05	n.q.	0.05
23.30	C2-Phenanthrene	206	C16H14	0.05	n.q.	0.05
23.45	Fluoranthene	202	C16H10	4.12	5.56	5.51
23.82	Phenanthro[4,5- <i>bcd</i>]thiophene	208	C14H8S	0.73	1.04	0.86
23.93	C3-Phenanthrene	220	C17H16	n.q.	n.d.	n.q.
24.00	Pyrene	202	C16H10	4.85	5.63	5.29
24.11	C3-Phenanthrene	220	C17H16	0.03	n.q.	n.q.
24.19	C3-Phenanthrene	220	C17H16	0.03	n.q.	n.q.
24.33	C3-Phenanthrene	220	C17H16	n.q.	n.d.	n.q.
24.44	C3-Phenanthrene	220	C17H16	n.q.	n.q.	n.q.
24.56	C1-Fluoranthene	216	C17H12	0.06	0.07	0.07
24.80	C1-Pyrene	216	C17H12	0.06	0.07	0.06
25.08	C1-Pyrene	216	C17H12	0.12	0.13	0.13
25.29	C1-Pyrene	216	C17H12	0.21	0.22	0.21
25.37	C1-Pyrene	216	C17H12	0.17	0.19	0.17
26.03	C2-Pyrene	230	C18H14	n.q.	n.q.	n.q.
26.06	C2-Pyrene	230	C18H14	n.q.	0.05	0.06
26.30	C2-Pyrene	230	C18H14	n.q.	n.q.	n.q.
26.33	Naphthalene, 1-(phenylmethoxy)-	234	C17H14O	n.d.	0.21	0.19
26.45	Benzo[<i>ghi</i>]fluoranthene	226	C18H10	0.08	0.10	0.11
26.62	C2-Pyrene	230	C18H14	0.04	0.05	0.04

Table 1 (continued)

Retention Time (minutes)	Aromatic Hydrocarbon	Molecular ion (<i>m/z</i>)	Formula	Concentration (ppm)		
				Kolang	Mukundpura	Aguas Zarcas
26.94	C2-Pyrene	230	C18H14	0.05	0.04	0.04
26.96	Benz[<i>a</i>]anthracene	228	C18H12	0.06	0.09	0.09
27.02	Triphenylene	228	C18H12	0.05	0.05	0.06
27.06	Chrysene	228	C18H12	0.07	0.09	0.09
27.27	Benzo[<i>c</i>]phenanthrene	228	C18H12	0.38	0.29	n.q.
30.41	Benzopyrene	252	C20H12	n.d.	0.05	0.05
31.50	Perylene	252	C20H12	n.d.	0.05	0.04
Total (ppm)				21.95	34.45	24.62
PAH detected				75	77	77
PAH quantified				68	67	61

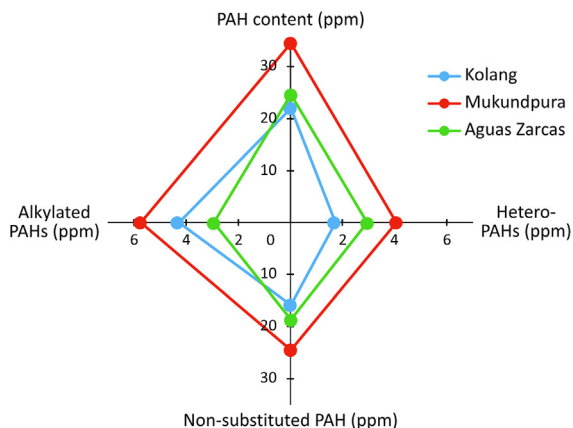


Fig. 2. Contents in ppm of the total PAHs (top axis), the alkylated PAHs (left axis), hetero-PAHs (mainly O and S-containing PAHs) in the right axis and non-substituted PAHs (bottom axis).

3.4. Compound specific carbon isotope ratios

The carbon isotopic composition of the most abundant PAHs is comprised between 0‰ for naphthalene and –15‰ for pyrene, with phenanthrene and fluoranthene exhibiting $\delta^{13}\text{C}_{\text{PDB}}$ values of about –10‰ and –5‰, respectively (Table 3 and Fig. 5). The carbon isotopic compositions for phenanthrene, fluoranthene and pyrene are similar to those reported for Murchison (Sephton et al., 1998; Gilmour and Pillinger, 1994; Huang et al., 2015), A-881458, an Antarctic CM2 chondrite (Naraoka et al., 2000) and LON 94101 (Huang et al., 2015). The isotope composition of naphthalene is not consistent with previous reports, though; this may be the consequence of terrestrial contamination for the lowest values (typical terrestrial values for naphthalene is –25‰ - O'malley et al., 1994).

3.5. Compound specific hydrogen isotope ratios

In addition to their low abundance in CCs, the low H content of chondritic PAHs makes the determination of their hydrogen isotope composition challenging. Here, we successfully measured the D content of the two most abundant PAHs detected in the CMs investigated, i.e. fluoranthene and pyrene (Fig. 6 and Table 3). Fluoranthene is systematically more depleted in D than pyrene, with $\delta\text{D}_{\text{VSMOW}}$ values of about –250‰ for fluoranthene vs $\delta\text{D}_{\text{VSMOW}}$ values comprised between –150 and –220‰ for pyrene.

4. Discussion

4.1. An interstellar origin for PAHs in CMs?

Recent laboratory experiments have evidenced that hydrothermal alteration conditions may trigger the production of relatively

high molecular weight, cyclized organic compounds such as PAHs from simple organic compounds via multiple condensation/polymerization reactions (Cody et al., 2011; Kebukawa et al., 2013, 2017, 2020; Kebukawa and Cody, 2015; Vinogradoff et al., 2018, 2020a, 2020b; Viennet et al., 2022). The hydrolysis of IOM could release soluble compounds including PAHs as well (Peltzer et al., 1984; Sephton et al., 1998; Oba and Naraoka, 2006; Huang et al., 2007; Yabuta et al., 2007; Aponte et al., 2011). Aqueous alteration episodes could thus have produced the PAHs measured here. This would be in line with the conclusions of the recent study conducted by Slavicinska et al. (2022) who reported that more altered CCs contain larger PAHs than more pristine CCs. Alternatively, such episodes could have destroyed PAHs, only leaving ‘intact’ the PAHs measured here. Theoretical calculations have shown that the formation of amino and carboxylic acids (such as acetic acid of glycine) from PAHs such as pyrene and fluoranthene is energetically favourable at probable parent-body alteration conditions (Yuen et al., 1984; Shock and Schulte, 1990).

Yet, the total PAH content of the CMs here does not display any correlation with the degree of alteration that they have experienced. Among the CMs investigated, the richest in PAHs is Mukundpura, i.e. neither the least nor the most altered one (Fig. 3 - Table 1). The same is true for hetero-PAHs, Mukundpura is the one containing the most O-PAHs and the least S-PAHs, and it contains as N-PAHs as Aguas Zarcas and Kolang (Fig. 3 - Table 1). Although a competition between production and destruction of PAHs could have occurred, leading to the measured PAH contents, it can alternatively be assumed that hydrothermal conditions did not impact the PAH content here. In that case, the measured PAHs were present at the time of meteorite parent-body formation, if not earlier.

A pre-accretion origin of PAHs would be in line with the earlier proposition made by Plows et al. (2003) based on the spatial distribution of PAHs in Murchison. According to these authors, the striking contrast in PAH content of the matrix and chondrules and the correlation between textural features and chemical gradients that they observed imply that no formation, migration, nor destruction of PAHs has occurred since their accretion (Plows et al., 2003). In a such scenario, i.e. a measured PAH content solely dictated by its initial quantity, the variability of PAH contents among CMs would suggest that PAHs were heterogeneously distributed within the parent body of CMs, possibly as a result of chromatographic separation (Wing and Bada 1991a, 1991b; Elsila et al., 2005). Although PAHs are considered insoluble in water, smaller ones may be more easily transported than bigger ones.

The PAHs measured here may have originated from a diversity of environments. In fact, PAHs are widely distributed throughout the cosmos (Cherchneff et al., 1992; Messenger et al., 1998; Dartois et al., 2004; Peeters et al., 2004; Dartois and Muñoz-Caro, 2007; Salama, 2008; Gredel et al., 2011; Bierbaum et al., 2011; Li and Draine, 2012; Woitke et al., 2016). PAHs are considered to be

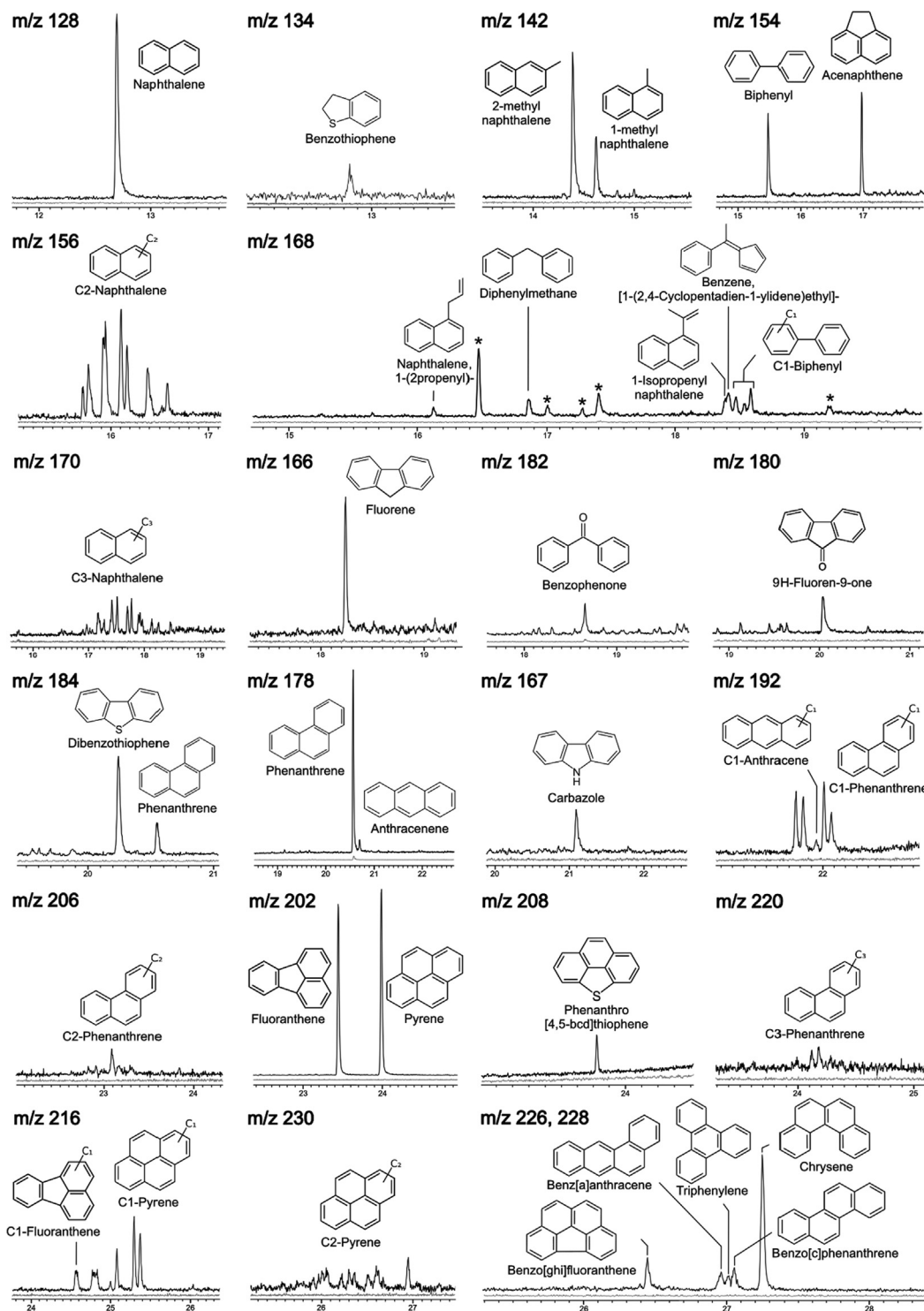


Fig. 3. Selective ion chromatograms for the DCM/MeOH extract of the CM1/2 Kolang meteorite and for blanks (in grey). Some large aliphatic hydrocarbons (*) can be identified at m/z 168.

the best candidates responsible for the IR feature observed in a variety of astrophysical environments, including the ISM (Allamandola et al., 1987, 1989), planetary nebulae (Cohen and Barlow, 2005), reflection nebulae (Joblin et al., 1996), HII regions (Bregman et al., 1989) and galactic nuclei (Willner et al., 1977). Laboratory simulations suggest that the synthesis of PAHs in the ISM involves the processing of simple gas-phase molecules (Sagan and Khare, 1979) and interstellar dust mantles (Greenberg

et al., 2000) by ultraviolet (UV) light. PAHs may also be formed in circumstellar outflows of asymptotic giant branch (AGB) stars (see Tielens and Charnley, 1997 for a review). Splitting of graphite grains (Tielens et al., 1987), accretion of carbon cations (Puget and Léger, 1989), and ion–molecule reactions (Herbst, 1991) have also been proposed as synthetic pathways.

Here, the carbon isotopic composition of the PAHs extracted from the CMs investigated may help constraining their origin.

Table 2

Relative proportions of parent PAHs and their alkylated products. For alkylated PAHs, concentrations of all isomers are added up and then normalized to the total concentration of this PAH (Σ PAH = parent + alkylated PAHs).

PAH	Relative proportion	Kolang CM 1/2	Mukundpura CM 2.0	Aguas Zarcas CM 2.2
Naphthalene	Naph/ Σ Naph	0.30	0.49	0.65
	C1-Naph/ Σ Naph	0.20	0.14	0.14
	C2-Naph/ Σ Naph	0.30	0.27	0.17
	C3-Naph/ Σ Naph	0.20	0.10	0.05
Biphenyl	Biph/ Σ Biph	0.60	0.68	0.74
	C1-Biph/ Σ Biph	0.40	0.32	0.26
Phenanthrene	Ph/ Σ Ph	0.70	0.84	0.77
	C1-Ph/ Σ Ph	0.19	0.14	0.15
	C2-Ph/ Σ Ph	0.09	0.02	0.07
	C3-Ph/ Σ Ph	0.02	0.00	0.00
Anthracene	An/ Σ An	0.78	0.85	0.87
	C1-An/ Σ An	0.22	0.15	0.13
Fluoranthene	Fluo/ Σ Fluo	0.98	0.99	0.99
	C1-Fluo/ Σ Fluo	0.02	0.01	0.01
	Py/ Σ Py	0.88	0.88	0.88
Pyrene	C1-Py/ Σ Py	0.10	0.10	0.10
	C2-Py/ Σ Py	0.02	0.02	0.02

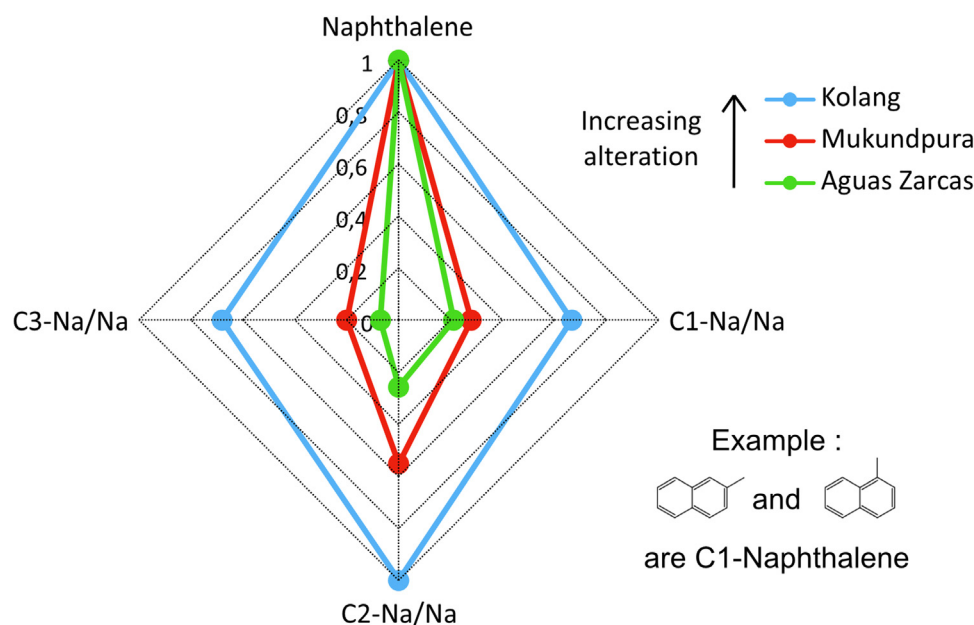


Fig. 4. Naphthalene alkylation series in CMs Kolang, Mukundpura and Aguas Zarcas. In these spider graphs, each spoke represents alkylated species and their distance to the center depends on their concentration. For one point, concentrations of alkylated isomers (both C1-Naphthalene in the example) are added up and normalized to the concentration of the unalkylated parent PAH (here naphthalene).

Table 3

Carbon and hydrogen isotope values in $\delta^{13}\text{C}_{\text{PDB}} \text{‰}$ and $\delta\text{D}_{\text{VSMOW}} \text{‰}$ for 4 and 2 PAHs in Kolang, Mukundpura, Aguas Zarcas. Error bars correspond to standard deviation calculated on 3 to 6 injections of the same extract.

PAH	Kolang (CM1/2)		Mukundpura (CM2)		Aguas Zarcas (CM2)	
	$\delta^{13}\text{C}_{\text{PDB}} \text{‰}$	$\delta\text{D}_{\text{VSMOW}} \text{‰}$	$\delta^{13}\text{C}_{\text{PDB}} \text{‰}$	$\delta\text{D}_{\text{VSMOW}} \text{‰}$	$\delta^{13}\text{C}_{\text{PDB}} \text{‰}$	$\delta\text{D}_{\text{VSMOW}} \text{‰}$
Naphthalene	-0.7 ± 0.6		2.3 ± 0.6		0.5 ± 1.6	
Phenanthrene	-10.5 ± 0.5		-8.6 ± 0.2		-11.0 ± 1.0	
Fluoranthene	-4.8 ± 0.3	-263 ± 18	-5.2 ± 0.4	-250.1 ± 9.1	-4.9 ± 0.8	-231.4 ± 17.8
Pyrene	-14.7 ± 0.2	-219.5 ± 9.5	-14.0 ± 0.5	-153.1 ± 10.3	-14.8 ± 0.6	-187.5 ± 8.6

Although they share the same elemental composition ($\text{C}_{16}\text{H}_{10}$), the fluoranthene and pyrene extracted here do not exhibit the same ^{13}C values. This difference suggests that these PAHs formed under kinetic control rather than by thermodynamic equilibrium (Naraoka et al., 2000). Here, the ^{13}C values of the PAHs of the pyrene series (i.e. naphthalene, phenanthrene and pyrene) are anticor-

related with their size (or their number of carbons, or their number of cycles, or their H/C). Hence, the more peri-condensed, the more depleted in ^{13}C the PAHs are. This suggests that the larger peri-condensed PAHs are rather formed from the smaller homologs via cycle addition. A similar isotopic trend was reported for PAHs in Murchison (Gilmour and Pillinger 1992, 1994) and A-881458

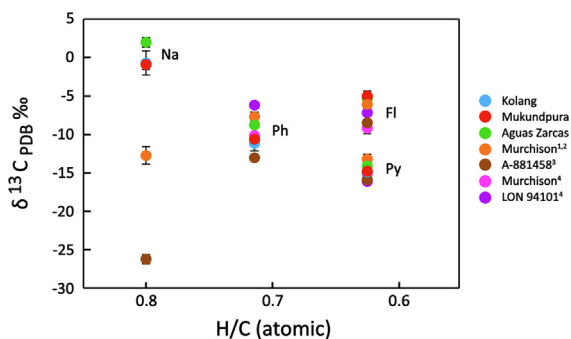


Fig. 5. $\delta^{13}\text{C}_{\text{PDB}}$ values (in ‰ vs PDB) of non-alkylated naphthalene (Na), phenanthrene (Ph), fluoranthene (Fl) and pyrene (Py) from Kolang, Mukundpura and Aguas Zarcas, Murchison, A-881458 and LON 94101. Error bars represent standard deviations. (1) Sephton et al., 1998; (2) Gilmour and Pillinger, 1994; (3) Naraoka et al., 2000; (4) Huang et al., 2015.

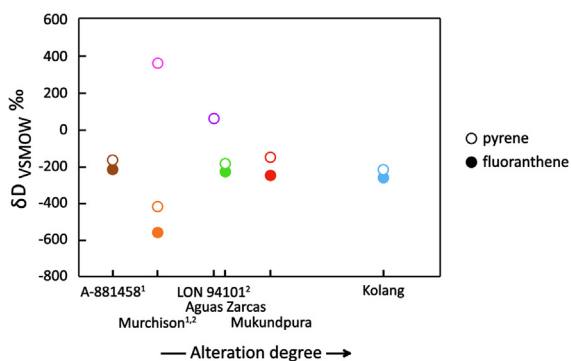


Fig. 6. $\delta\text{D}_{\text{VSMOW}}$ values (in ‰ vs VSMOW) of pyrene and fluoranthene from the CMs Kolang, Mukundpura, Aguas Zarcas, Murchison, A-881458 and LON 94101. Error bars are smaller than symbols. (1) Oba and Naraoka, 2003 (brown and orange); (2) Huang et al., 2015 (pink and purple). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(Naraoka et al., 2000). Of note, Naraoka et al. (2000) distinguished two reaction pathways, i.e. the ‘pyrene series’ and the ‘fluoranthene series’, explaining the difference between the ^{13}C values of pyrene and fluoranthene. No terrestrial environment enables this large kinetic fractionation, occurring under low-temperature conditions in the interstellar medium or onto meteorite parent-bodies (Naraoka et al., 2000).

4.2. Impact of secondary processes

4.2.1. Alkylation

The three CMs contain alkylated PAHs (PAH-(CH₂)_n) (Table 2). Hydrothermal processes occurring on Earth may lead to the production of alkylated PAHs together with unsubstituted PAHs (Gieskes et al., 1988; Kawka and Simoneit, 1990), the latter predominating over their alkyl-substituted homologs as in combustion products (Youngblood and Blumer, 1975; Wakeham et al., 1980). However, alkylated PAHs may form from unsubstituted PAHs in the ISM. In fact, in addition to PAHs, simple alkanes such as methane and ethane have been identified in both the gas phase of the ISM and in interstellar ices (Lacy et al., 1991). Exposure of interstellar ices to UV radiation may lead to the production of more complex compounds via photochemical processes (Bernstein et al., 1995; McDonald et al., 1996; Greenberg et al., 2000; Danger et al.,

2013). In particular, alkylated PAHs and/or hetero-PAHs may form under vacuum at very low temperatures via photoreactions involving PAHs and alkanes exposed to UV radiation as demonstrated experimentally (Bernstein et al., 2002; Mahajan et al., 2003).

Another scenario could involve the production of alkylated PAHs from unsubstituted PAHs in water, at temperatures typical of asteroidal conditions (Mahajan et al., 2003). An increasing PAH alkylation was found to be correlated with increasing aqueous exposure of carbonaceous chondrite parent bodies, but was interpreted then as the result of the higher relative solubility and vapor pressure of simple PAHs versus their alkylated counterparts (Wing and Bada 1991a, 1991b; Elsila et al., 2005). As unalkylated PAHs migrate more effectively than alkylated ones, a more intense aqueous alteration would favour their preferential chromatographic separation and removal, leading to a relative enrichment in alkylated PAHs (Shiu and Ma, 2000; Elsila et al., 2005). The favoured migration for unalkylated PAHs would explain the relatively high levels of alkylation reported for CM2 chondrites (Pering and Ponnampuruma, 1971; Hahn et al., 1988; Wing and Bada 1991a, 1991b). Even higher levels of alkylation were reported for CV3 and CO3 meteorites having experienced metamorphism (Elsila et al., 2005) and for Antarctic micrometeorites (Clemett et al., 1998). These observations on objects having experienced higher temperatures than CMs were interpreted as the result of a preferential volatilization of unalkylated PAHs with increasing thermal exposure (Clemett et al., 1998; Elsila et al., 2005).

Here, the degree of naphthalene alkylation is positively correlated with the intensity of alteration experienced by the CMs investigated, with Kolang exhibiting a greater abundance of alkylated naphthalene than Mukundpura and Aguas Zarcas (Fig. 3). According to the index of alkylation proposed by Clemett et al. (1998), the values in the case of naphthalene are 0.58, 0.25 and 0.12 for Kolang, Mukundpura and Aguas Zarcas. Such alkylation trend is consistent with previous interpretations where a more pronounced chromatographic separation with increasing exposure to water is responsible for the preferential migration and loss of unsubstituted PAHs (Hahn et al., 1988; Wing and Bada 1991a, 1991b; Elsila et al., 2005), in respect to their alkylated homologs. Surprisingly, no alkylated compounds were detected in the CM2 Paris by Martins et al. (2015). Paris has indeed experienced very little aqueous alteration (Marrocchi et al., 2014; Hewins et al., 2014; Vinogradoff et al., 2017), and while the level of alkylation is expected to be low, it should be non-zero, if both unsubstituted and alkylated PAHs are produced in the ISM and accreted together onto the CM parent-body. Plus, as discussed above, the total PAH content of the three CMs investigated here does not display any correlation with the degree of alteration that they experienced. A production of alkylated PAHs from unsubstituted PAHs during hydrothermal processes on parent-bodies would reconcile this absence of alkylated PAHs in Paris. It would also explain the absence of correlation between the total PAH content and the degree of alteration, as well as the positive correlation between the degree of naphthalene alkylation and the intensity of alteration of CMs observed here.

4.2.2. D/H values

The most abundant PAHs measured here exhibit a surprisingly low deuterium content, with $\delta\text{D}_{\text{VSMOW}}$ values of about -250‰ for fluoranthene and $\delta\text{D}_{\text{VSMOW}}$ values comprised between -150 and -220‰ for pyrene (Fig. 5). Yet, most interstellar chemical processes such as ion-molecule reactions, catalytic gas-grain reaction on grain surfaces or radiation processing will lead to the produc-

tion of species significantly enriched in D (Tielens 1983; 1997; Bernstein et al., 1995, 1999; Millar et al., 2000; Sandford et al., 2000, 2001; Messenger et al., 2006; Le Guillou et al., 2013). The process of unimolar photodissociation, restricted to molecular species like PAHs that can absorb a high-energy photon without being destroyed, will occasionally shed a peripheral H atom if the absorbed energy is large enough. The repeated loss and capture of peripheral H atoms, combined with the difference in H and D zero-point energies can lead to D enrichment. (Allamandola et al., 1989; Sandford et al., 2000). Thus, the PAHs formed in the ISM should exhibit D enrichments, which is not the case of the PAHs extracted from the CMs investigated here.

Isotope exchange with a D-poor water was proposed to explain the lower D-content of the IOM of CIs and CMs compared to that of the IOMs of CRs (Alexander et al., 2010) even though each class of CCs did not accrete organics with similar initial δD values (Remusat et al., 2010). It has been shown experimentally that PAHs may experience hydrogen isotopic exchange (Alexander et al., 1982; Sessions et al., 2004). Furthermore, Piani et al. (2021) recently reported that Mukundpura and Aguas Zarcas have seen water with similar negative δD values (-422‰ and -377‰ , respectively). Isotope exchange with water could thus explain the observed depletion in D of the PAHs measured here, assuming that the PAHs accreted by the CMs investigated here shared initially identical δD values.

Previously, Oba and Naraoka (2003) reported extremely negative δD values for Murchison (a CM2.5 - $\delta D_{\text{VSMOW}} = -421$ and -560‰ for pyrene and fluoranthene, respectively) and values similar to ours for A-881458 (a poorly altered CM2 - $\delta D_{\text{VSMOW}} = -168$ and -219‰ , respectively). In contrast, Huang et al. (2015) reported positive δD values for pyrene in Murchison ($\delta D_{\text{VSMOW}} = +357\text{‰}$) and LON 94101 (a CM2.2-2.3 - $\delta D_{\text{VSMOW}} = +57\text{‰}$ - Fig. 6). Although these studies are not consistent with each other concerning Murchison, δD values of PAHs measured in less altered CMs are enriched compared to Mukundpura, Aguas Zarcas and Kolang, strengthening the hypothesis of isotope exchange with water during aqueous alteration episodes. Here, with the exception of pyrene in Mukundpura, the δD values of the PAHs define a negative trend with the degree of alteration experienced by the CMs (Fig. 6). Also, the difference in δD values between fluoranthene and pyrene for each of the CM suggests that isotope exchange did not reach equilibrium, even for Kolang, because of a too short duration of exposure to water, or a too low temperature. Fluoranthene being slightly more soluble than pyrene (Mackay and Shiu, 1977), it may be more prone to isotope exchange, explaining its lower D content. The specific case of pyrene in Mukundpura may result from its initial heterogeneous distribution. In fact, as discussed above, the PAHs may have been heterogeneously distributed within the parent body of CMs, possibly as a result of chromatographic separation (Wing and Bada 1991a, 1991b; Elsila et al.,

2005). Pyrene in Mukundpura may have been exposed to less water, explaining its higher D-content.

5. Conclusions

We detected more than 75 PAHs in the recently recovered CMs Kolang, Mukundpura and Aguas Zarcas, with PAH sizes ranging from 2 (naphthalene) to 5 cycles (benzopyrene). We also detected hetero-PAHs (mainly O and S-containing PAHs), alkylated compounds and we measured carbon and hydrogen isotope ratio for some of the most abundant PAHs. Even though PAHs were previously proposed to be potentially produced through alteration on the parent-body, their carbon isotope signature and their PAH content versus alteration are pointing towards a pre-accretionary origin for PAHs, via cycle addition, occurring likely in the ISM. Nevertheless, the content of alkylated PAHs seems correlated to the degree of alteration in the three CMs, despite no correlation between the total PAH content and the degree of alteration. Our results show that the hypothesis for a production of alkylated PAHs during hydrothermal events may explain our observations as well as the absence of alkylated PAHs in Paris. All these results account for the importance of PAHs to help trace both pre-accretion and secondary processes in carbonaceous chondrites. Finally, while PAHs are thought to be deuterium-rich in the ISM, we measured for fluoranthene and pyrene a low deuterium content pointing towards hydrogen exchange with deuterium-depleted water during aqueous alteration. This hypothesis is strengthened by the recent measurement of depleted chondritic water in CMs and the correlation between PAH δD values and the degree of alteration.

Data availability

Data will be made available on request.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Non-PAH compounds

Table A1

Non-PAH compounds detected in the GC-MS chromatograms of the meteorites Kolang, Mukundpura, Aguas Zarcas and in the blank. Peaks in the blank are contaminants coming from solvents or materials, others are indigenous or contaminants. When possible, $\delta^{13}\text{C}_{\text{PDB}} \text{‰}$ (left) and $\delta\text{D}_{\text{VSMOW}} \text{‰}$ (right) values are displayed. Alkane isotopic values are in the same range than terrestrial ones (Sephton et al., 2001), being potential contamination (Oró et al., 1968; Krishnamurthy et al., 1992; Sephton et al., 2001; Pizzarello et al., 2001; Sephton, 2014; Lee et al., 2021).

Retention time (GC-MS)	Compound	Kolang	Mukundpura	Aguas Zarcas	Blank
11.06	Trimethyldecane	+	+	+	+
11.52	Cyclopentasiloxane, decamethyl-	+	+	+	+
13.80	Unidentified alkane		+		
14.08	Cyclohexasiloxane, dodecamethyl-	+	+	+	+
14.16	Octodecane 6 methyl		-30.2 ± 0.7	-32.7 ± 4.3	
14.29	Undecanal	+	+		
14.47	Unidentified alkane		+		
15.21	Unidentified alkane	+		+	
15.55	Phenol,4-(1,1-dimethylpropyl)-	+	-29.5 ± 1.8	-33.7 ± 2.2	
15.69	Unidentified alkane	-29.7 ± 2.3 ; -189.5 ± 63	-28.4 ± 2.1 ; -129.5 ± 19	-32.3 ± 4.3 ; -107.0	
16.51	1-undecanol	-30.0 ± 1.7 ; -216.2 ± 34	-29.8 ± 1.7 ; -170.2 ± 62	-30.2 ± 0.1 ; -156.0 ± 35	
16.71	Tetradecane, 2,6,10-trimethyl-				
16.96	Phenol, 3,5-bis(1,1-dimethylethyl)-	+	+	+	+
17.52	Hexathiane	+	+	+	
17.87	Benzoic acid, 4-methyl-, [4-(methoxycarbonyl)phenyl]methyl ester			+	
18.06	Unidentified alkane	-29.0 ± 0.6		-31.6 ± 0.9	
19.21	Unidentified alkane	+	+	+	
21.87	Diphenyl sulfone	+	+	+	+
22.14	Unidentified alkane/phenyl		+		
22.55	Unidentified alkane/phenyl	-33.6 ± 1.9 ; -195.7 ± 48	-32.9 ± 1.7 ; -132.6 ± 88		
24.13	Phenol, 4,4'-(1-methylethylidene)bis-	+	+	+	+

Appendix B. Supplementary material

Supplementary material to this article can be found online at <https://doi.org/10.1016/j.gca.2022.08.039>.

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