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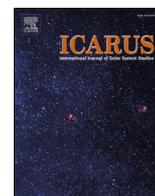
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# Influence of hydrothermal asteroidal conditions on the molecular structure and isotopic compositions of polycyclic aromatic hydrocarbons

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## ABSTRACT

A variety of polycyclic aromatic hydrocarbons (PAHs) are reported in carbonaceous chondrites (CCs) and in the interstellar medium (ISM). Although PAHs in CCs are not as large as those detected in the ISM, their carbon isotope composition is interpreted as pinpointing an interstellar origin. In contrast, their hydrogen isotope composition can be related to the extent of secondary processes, as is the proportion of alkylated PAHs within CCs. Here, we experimentally investigate the molecular and isotopic evolution of PAHs under simulated asteroidal hydrothermal conditions at 150 °C. Results show that PAHs are chemically stable under these conditions whatever their size, i.e. no destruction, conjugation nor alkylation occurs, even in the presence of other reactive organic molecules. Plus, PAHs retain their carbon isotope compositions even in the presence of another carbon-rich reservoir, either organic or inorganic. On the other hand, their hydrogen isotope composition is modified through exchange with water. Of note, as shown by additional experiments, the presence of smectites, abundant in CCs, impacts the relative abundances of extractable PAHs, saponite trapping more efficiently the larger PAHs. Altogether, results of the present experiments show that PAHs of CCs can be used as tracers of both pre-accretion and secondary processes.

## 1. Introduction

Organic matter in chondrites is usually divided into an insoluble fraction (IOM - 50 to 90 wt%) and a soluble fraction (SOM - 10 to 50 wt%). While the IOM consists in a reticulated macromolecule made of aromatic units interconnected by short and branched aliphatic chains (Derenne and Robert, 2010; Vinogradoff et al., 2017), the SOM is a mixture of diverse soluble compounds such as carboxylic acids, amino acids, nucleobases (Pizzarello, 2006; Remusat, 2015; Martins et al., 2015) and polycyclic aromatic hydrocarbons (PAHs - Naraoka et al., 2000; Lecasble et al., 2022). PAHs are organic molecules consisting of two or more fused benzene rings (Richter and Howard, 2000; Abdel-Shafy and Mansour, 2016) and their size in CCs range from 2 rings (naphthalene - 10C atoms) to 7 rings (coronene - 24C atoms) (Slavcinska et al., 2022; Sabbah et al., 2017, 2022). The PAHs detected in CCs may originate from the interstellar medium (ISM), as previously suggested (Plows et al., 2003). In fact, PAHs are abundant and ubiquitous in the ISM, representing up to 20% of the total carbon (Leger and Puget, 1984; Allamandola et al., 1985, 1989; Tielens, 2008). These PAHs could have formed either via the irradiation of simple gas-phase molecules and

interstellar dust mantles by ultraviolet (UV) light or via reactions in circumstellar outflows of asymptotic giant branch (AGB) stars (Sagan and Khare, 1979; Cherchneff et al., 1992; Tielens and Charnley, 1997; Greenberg et al., 2000).

### 1.1. Degradation/polymerization of PAHs

Yet the presence, in CCs, of PAHs inherited from the ISM remains a subject of debate, in particular because sizes do not match. Chondritic PAHs have a maximum size of ~24C atoms (Sabbah et al., 2017, 2022) while interstellar PAH sizes range from 50 carbon atoms (Tielens, 2008, 2011) to thousands of carbon atoms (Allamandola et al., 1989; Pendleton and Allamandola, 2002). This discrepancy could result from secondary processes having modified all the constituents of CCs (Brearley, 2006; Cody et al., 2011; Le Guillou and Brearley, 2014; Vinogradoff et al., 2018; Viennet et al., 2022; Suttle et al., 2021). In fact, almost all the CCs have experienced aqueous alteration episodes, mostly triggered by the melting of ice due to the radioactive decay of short-lived radionuclides such as <sup>26</sup>Al (McSween, 1979; Brearley, 2006; Krot et al., 2006; Verdier-Paoletti et al., 2017; Fujiya, 2018), but also possibly by

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impact heating, solar heating, or atmospheric ablation (Turner et al., 2021). Although it has been proposed that PAHs are inherited from the ISM (Yang and Epstein, 1983, 1984; Kerridge, 1983; Allamandola et al., 1987), Shock and Schulte (1990) predicted that, if exposed to hydrothermal conditions, PAHs would break down, leading to the production of carboxylic and amino acids. Experimental data on the stability of PAHs under hydrothermal conditions are thus required to provide new constraints on the origin of PAHs in CCs.

### 1.2. Alkylation of PAHs

The abundance of alkylated PAHs in CCs, i.e. PAHs with side chains containing up to 4 additional carbon atoms (Pering and Ponnampuram, 1971; Hahn et al., 1988) constitute an interesting point to consider. It has been suggested that a chromatographic separation of alkylated and non-alkylated PAHs occurs during aqueous alteration on the parent body. As alkylated PAHs are less soluble than non-alkylated equivalents, this may explain the larger relative amount of alkylated PAHs with respect to non-alkylated equivalent in more altered CCs (Wing and Bada, 1991a, 1991b; Shiu and Ma, 2000; Elsila et al., 2005; Lecasble et al., 2022). However, no alkylated PAHs were detected in the Paris meteorite, a weakly altered CM (Martins et al., 2015), suggesting that alkylated PAHs could rather be produced during aqueous alteration events. Experimental data on the alkylation of PAHs under hydrothermal conditions are thus required to provide new constraints on the origin of alkylated PAHs and their proportion in CCs.

### 1.3. Carbon isotope evolution

The carbon isotope signature of PAHs has also been investigated. The PAHs in CCs exhibit carbon isotope compositions defining two negative trends (i.e. the pyrene and the fluoranthene series) with increasing PAH size (larger PAH have lower  $\delta^{13}\text{C}$  values - Sephton et al., 1998; Gilmour and Pillinger, 1994; Naraoka et al., 2000; Huang et al., 2015; Lecasble et al., 2022). This has been interpreted as resulting from the production of these PAHs via cycle addition having occurred at very low temperature, i.e. before their accretion onto parent bodies (Gilmour and Pillinger, 1994; Naraoka et al., 2000). Since almost all the CCs have experienced aqueous alteration episodes, the preservation of these signatures implies that the carbon isotope composition of PAHs can withstand hydrothermal conditions. However, this has not been demonstrated experimentally, yet. Experimental data on the evolution of the carbon isotope compositions of PAHs under hydrothermal conditions in the presence of other carbon reservoirs are thus required.

### 1.4. Hydrogen isotope evolution

In contrast to the carbon isotope composition, the deuterium isotope composition of PAHs in CCs does not pinpoint an interstellar origin. In fact, the PAHs in the ISM are expected to be D-rich (Millar et al., 2000; Peeters et al., 2004; Salama, 2008), with D enrichment resulting from unimolecular photodissociation (Allamandola et al., 1987, 1989), gas phase ion-molecule reactions (Dalgarno and Lepp, 1984) or gas-grain reactions (Tielens and Charnley, 1997; Sandford, 2002). In contrast, the PAHs in CCs are D-poor compared to other organic compounds such as amino acids (Oba and Naraoka, 2003; Elsila et al., 2012; Huang et al., 2015; Lecasble et al., 2022; Graham et al., 2022). While these low contents in D have been interpreted by some authors as inherited from interstellar conditions (Huang et al., 2015; Graham et al., 2022), Lecasble et al. (2022) interpreted these values as the consequence of hydrogen isotope exchange with D-poor water during aqueous alteration episodes. Consistently, Alexander et al. (1982) showed that PAHs are sensitive to D-exchange in dry conditions, and Oba and Naraoka (2003) showed that such process can occur in acidic aqueous conditions. However, the parent bodies of CCs have experienced aqueous alteration under rather basic conditions (Zolotov, 2012; Takir et al., 2013; Suttle

et al., 2021, 2022). It thus remains to demonstrate that PAHs may experience D-exchange under such conditions.

A last point worth to investigate is the possible influence of clay minerals. CCs are rich in clay minerals (Pearson et al., 2006; Garvie and Buseck, 2007; Le Guillou and Brearley, 2014; Yesiltas and Kebukawa, 2016; Changela et al., 2018) and it has been shown that clay minerals may influence organic reactions (cyclization, dehydration, Michael-addition and IOM formation – Vinogradoff et al., 2020a, 2020b; Vienne et al., 2022). Besides some rare studies having shown that the presence of montmorillonite could enhance PAH substitution and polymerization (Hagiwara et al., 2000; Watson and Sephton, 2015) and that serpentine does not produce new PAHs (Giese et al., 2019), no laboratory experiments have been conducted to investigate the effect of saponite (the most abundant clay mineral in CCs with serpentine - Brearley, 2006) on PAHs under hydrothermal conditions typical of asteroids.

Here, we report series of laboratory experiments specifically designed to investigate the molecular and isotopic evolution of PAHs under hydrothermal conditions simulating aqueous alteration events having occurred within/onto carbonaceous asteroids. Experiments were conducted under hydrothermal conditions at 150 °C with phenanthrene (3 rings – 178 amu), pyrene (4 rings – 202 amu), coronene (7 rings – 300 amu) and graphene, in the presence of other organic carbon reservoirs (hexane, glycine, acetic acid), in the presence of  $^{13}\text{C}$ -enriched compounds, either organic or inorganic (glycine, graphitic carbon and carbonates), in the presence of  $\text{D}_2\text{O}$  and in the presence of pure saponite.

## 2. Materials and methods

### 2.1. Starting materials

Most of the starting materials were provided by Sigma Aldrich: Phenanthrene (>99.5%), pyrene (98%), coronene (97%), graphene nanoplatelet (powder),  $\text{D}_2\text{O}$  (99.9 atom % D), carbon- $^{13}\text{C}$  (99 atom %  $^{13}\text{C}$ ), calcium carbonate- $^{13}\text{C}$  (99 atom %  $^{13}\text{C}$ ), glycine (> 99%), acetic acid (> 99.7%), and glycine- $^{13}\text{C}_2$  (99 atom %  $^{13}\text{C}$ ). Hexane (>99%) was provided by Roth. The pure saponite used for the present experiments ( $\text{Na}_{0.4}(\text{Si}_{3.6}\text{Al}_{0.4})\text{Mg}_3\text{O}_{10}(\text{OH})_2$ ) was synthesized from a gel produced by mixing an  $\text{AlCl}_3$  solution, a  $\text{Na}_2\text{SiO}_3$  solution and a  $\text{MgCl}_2$  solution at 0.2 M, and exposed to 230 °C for 10 days. Saponite purity has been checked with XRD, FTIR and CHNS analysis. The mineral is pure and contains no carbon.

### 2.2. Experiments in reactors

Organic compounds (powdered) and minerals were loaded into 20 mL Parr® Ti-reactors under argon atmosphere (>99.9999%; Air Liquide, ALPHAGAZ 1) with 10 mL degassed bi-distilled water (Table 1). Water was degassed using Ar with the same purity. Reactors were maintained for 28 days at 150 °C (4.7 bars saturation vapor pressure). Gas present at 150 °C in reactors at the end of the experiment were identified and quantified by gas chromatography coupled with thermal conductivity detection (GC-TCD). Then, reactors were cooled down at room temperature and opened. Reactors were rinsed with dichloromethane (DCM). Extracts were dried and weighed for quantification. In the case of the experiment with saponite, samples were filtrated (vacuum driven glass filtration unit, 47 mm GSWP filters with 0.22  $\mu\text{m}$  pores – Merck Millipore), without sonication before drying. Non-polar organics like hydrocarbons were extracted and analysed by GC-FID for evaluation of PAH molecular evolution. Yields corresponds to ratio between starting and dried recovered organics.

### 2.3. Experiment in capsules

Some experiments were conducted in gold capsules due to the limited quantity of materials available (coronene, graphene,  $^{13}\text{C}$  glycine,

**Table 1**

List of the experiments conducted in the present study.

Experiments	Temperature	Duration	Container	Organics	Minerals	Water	Analysis	Yield
Phenanthrene + Pyrene (P/P)	150 °C	28 days	reactors	100 mg		10 mL	GC-TCD, GC-FID	98.2%
Coronene	150 °C	3 months	capsules	2.5 mg		100 µL	GC-FID	–
Graphene	150 °C	3 months	capsules	2.5 mg		100 µL	GC-FID	–
P/P + hexane	150 °C	28 days	reactors	50 mg + 50 mg		10 mL	GC-FID	97.4%
P/P + glycine	150 °C	28 days	reactors	50 mg + 50 mg		10 mL	GC-FID	98.2%
P/P + acetic acid	150 °C	28 days	reactors	50 mg + 50 mg		10 mL	GC-FID	97.2%
P/P + glycine <sup>13</sup> C	150 °C	7 days	capsules	5 mg + 45 mg		100 µL	GC-FID, GC-irMS	96.3%
P/P + graphitic carbon <sup>13</sup> C	150 °C	7 days	capsules	5 mg	45 mg	100 µL	GC-FID, GC-irMS	94.2%
P/P + calcium carbonate <sup>13</sup> C	150 °C	7 days	capsules	5 mg	45 mg	100 µL	GC-FID, GC-irMS	93.9%
P/P + D <sub>2</sub> O	150 °C	7 days	capsules	5 mg		100 µL	GC-FID, GC-irMS	97.9%
P/P + saponite	150 °C	28 days	reactors	100 mg	900 mg	10 mL	GC-TCD, GC-FID	84.6%

<sup>13</sup>C graphitic carbon, <sup>13</sup>C calcium carbonate and D<sub>2</sub>O). Three cm-long gold capsules were prepared from a 5.4 mm-large x 0.2 mm-thickness tube (Heraeus Deutschland GmbH & Co. KG). After introduction of the samples, water was added with a glass syringe in a glove box under argon atmosphere (> 99.9999% - Air Liquide ALPHAGAZ 1). Then, capsules were welded and put into 20 mL Parr® reactors in Ti filled with 5 mL of bi-distilled water and placed in an oven for 7 days or 3 months at 150 °C. Water was added to the reactors to prevent explosion of the capsules by maintaining a saturation vapor pressure of ~4.7 bar. At the end of the experiments, capsules were cleaned, opened and immersed in 5 mL of DCM. In the presence of minerals, samples were centrifuged. Organics were then analysed by GC-FID (Gas Chromatography-Flame Ionization Detector) to quantify phenanthrene and pyrene content and to check for potential molecular evolution. For isotope exchange, experiments were also performed following this setup.

#### 2.4. Gas Chromatograph – thermal conductivity detector (GC-TCD)

We used a Shimadzu GC-2014 equipped with a thermal conductivity detector (TCD-2014) operated at IMPMC, MNHN (Paris, France) for gas identification and quantification. After connection of the reactor, a < 0.01 bar vacuum was set in the sampling line using a DIVAC 1.4HV3C primary vacuum oil-free pump. Then, samples were injected in the GC through this sampling line. Ultra-high-quality argon (> 99.9999% - Air Liquide ALPHAGAZ 1) was used as carrier gas. Two columns, HayeSep Q (80/100 mesh, 1.8 m × 1/8 in., 2 mm) followed by a Molecular Sieve 13× (60/80 mesh, 1.8 m × 1/8 in., 2 mm), were combined for optimal gas separation. The reactor and the injection line were kept at 150 °C. After connection of the reactors but before their openings, blanks chromatograms were collected to rule out leaks on the line (named control run hereafter). During analysis, the GC oven temperature was kept at 60 °C during 3 min and then increased at 20 °C/min until 110 °C was reached then held 6 min. Gas mixtures provided by Air Products were used for calibration of partial pressures in the gas volume sent into the GC.

#### 2.5. Gas Chromatography-flame ionization detector analysis (GC-FID)

Phenanthrene and pyrene were analysed and quantified using an Agilent Technologies 7890B GC equipped 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-purity 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. The oven temperature was kept at 75 °C during 0.5 min and then increased at 20 °C/min until 250 °C was reached and held for 1 min. For coronene and graphene experiments, temperature was kept at 150 °C during 0.5 min and then increased at 30 °C/min until 300 °C was reached and held 5 min.

#### 2.6. Gas Chromatography-isotope ratio mass spectrometry analysis (GC-irMS)

Compound-specific carbon and hydrogen isotope analyses were performed on an Elementar VisION isotopic mass spectrometer interfaced with an Agilent Technologies 7890 B GC through a GC5 Furnace system, installed 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). For carbon analysis, 0.2 µL of each extract were injected at 280 °C in split mode with a ratio of 2. For hydrogen analysis, the injection volume was 5 µL. In both cases, the oven temperature was kept at 170 °C during 1 min and then increased at 20 °C/min until 280 °C was reached and held for 4 min. After the 4 min solvent delay, the products were directed through a 350 °C transfer line to the Elementar GC5 Furnace. For carbon-isotope analysis, organic molecules were oxidized in CO<sub>2</sub> thanks to a quartz tube packed with CuO/Pt wire set at 850 °C in. For hydrogen-isotope analysis, the GC5 was equipped with a ceramic tube operated at a temperature of 1250 °C, converting compounds into H<sub>2</sub>. Detector was operated at room temperature. The maximum uncertainties (on session standards or on samples) and the number of analysis are given. Results were corrected using international reference material: naphthalene ( $\delta^{13}\text{C}_{\text{PDB}} = -26.12 \pm 0.02 \text{ ‰}$ ,  $\delta\text{D}_{\text{VSMOW}} = -58.6 \pm 1.0 \text{ ‰}$ ) and phenanthrene ( $\delta^{13}\text{C}_{\text{PDB}} = -25.39 \pm 0.03 \text{ ‰}$ ,  $\delta\text{D}_{\text{VSMOW}} = -84.1 \pm 1.3 \text{ ‰}$ ) (Indiana University in Bloomington, USA – Schimmelmann et al., 1999). A session drift correction has been applied using in-house phenanthrene and pyrene standards and for hydrogen measurement, a H<sub>3</sub><sup>+</sup> correction was calculated and applied (Sessions et al., 2001). In the following, hydrogen isotopic ratios are expressed as isotope abundance (D/(D + H)), while carbon isotopic ratios are expressed in the  $\delta$  notation relative to the international Pee Dee Belemnite standard following the equation:

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

### 3. Results

#### 3.1. Experiments with phenanthrene and pyrene

We conducted experiments with phenanthrene and pyrene at 150 °C for 28 days (Table 1). At the end of the experiments, no C-containing permanent gas was detected in the gas phase as revealed by GC-TCD (Fig. 1). The solvent extract of the residues of the experiments contain both pyrene and phenanthrene as revealed by GC-FID (Fig. 2), in relative amounts similar to those of the starting materials (98.2% of the initial pyrene and phenanthrene compounds were recovered at the end of the experiments). The missing PAHs were likely lost during the extraction procedure and sample handling.

#### 3.2. Experiments with coronene and graphene

Similar experiments in simulated asteroidal conditions have been

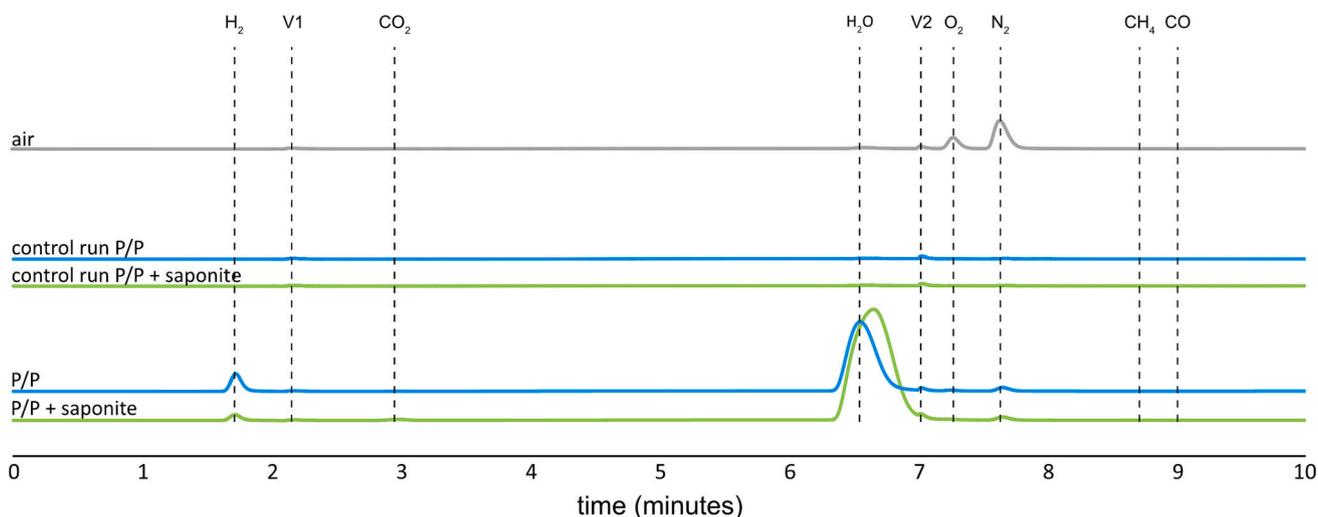


Fig. 1. GC-TCD chromatograms of the gas phase of the experiments conducted in reactors (28 days). Also shown are the chromatograms of the air and control runs conducted before the openings of the reactors. V1 and V2 are peaks corresponding to valve rotations. Vertical scales are equal.

conducted with coronene and graphene at 150 °C for 3 months (Table 1). The solvent soluble products of the experiments conducted with coronene only contain coronene and benzo[ghi]perylene, a minor contaminant already detected in the starting materials (Fig. 2). The quantification is complicated as coronene compounds do not elute properly. There is no solvent soluble compound detected in the experiments conducted with graphene, nor in the starting materials since graphene is not soluble at all and free of contaminant (Fig. 2).

### 3.3. Experiments with reactive and small molecules

Experiments with phenanthrene and pyrene have also been conducted at 150 °C for 28 days in the presence of reactive organic compounds, namely hexane, glycine and acetic acid (Table 1). The solvent soluble extracts of the experimental products contain both pyrene and phenanthrene as revealed by GC-FID (Fig. 2), in relative amounts similar to those of the starting materials (97.6% of the initial pyrene and phenanthrene compounds were recovered at the end of the experiments). The starting reactive organic compounds are not detected. Hexane may be diluted in the DCM peak and both glycine and acetic acid are either not extracted with DCM or not eluted with our non-polar HP-5 GC column. No new hydrocarbons are detected.

### 3.4. Experiments with $^{13}\text{C}$ -enriched materials

Experiments with phenanthrene and pyrene have also been conducted at 150 °C for 7 days in the presence of  $^{13}\text{C}$ -enriched organic or inorganic compounds, namely glycine, graphitic carbon and calcium carbonate (Table 1). The solvent extract of the experimental residues contains both pyrene and phenanthrene as revealed by GC-FID (Fig. 2), in relative amounts similar to those of the starting materials (94.8% of the initial pyrene and phenanthrene compounds were recovered at the end of the experiments). Most important, the  $\delta^{13}\text{C}_{\text{PDB}}$  values of the recovered pyrene and phenanthrene compounds were identical (within error bars) to those of the starting materials (Table 2 – Fig. 3).

### 3.5. Experiment with perdeuterated water

Experiments with phenanthrene and pyrene have also been conducted at 150 °C for 7 days in the presence of pure  $\text{D}_2\text{O}$  (Table 1). The solvent extract of the residues of these experiments contain both pyrene and phenanthrene as revealed by GC-FID (Fig. 2), in relative amounts similar to those of the starting materials (97.9% of the initial pyrene and phenanthrene compounds were recovered at the end of the

experiments). Interestingly, the D abundance of the recovered pyrene and phenanthrene compounds are significantly higher than those of the starting materials (Table 3).

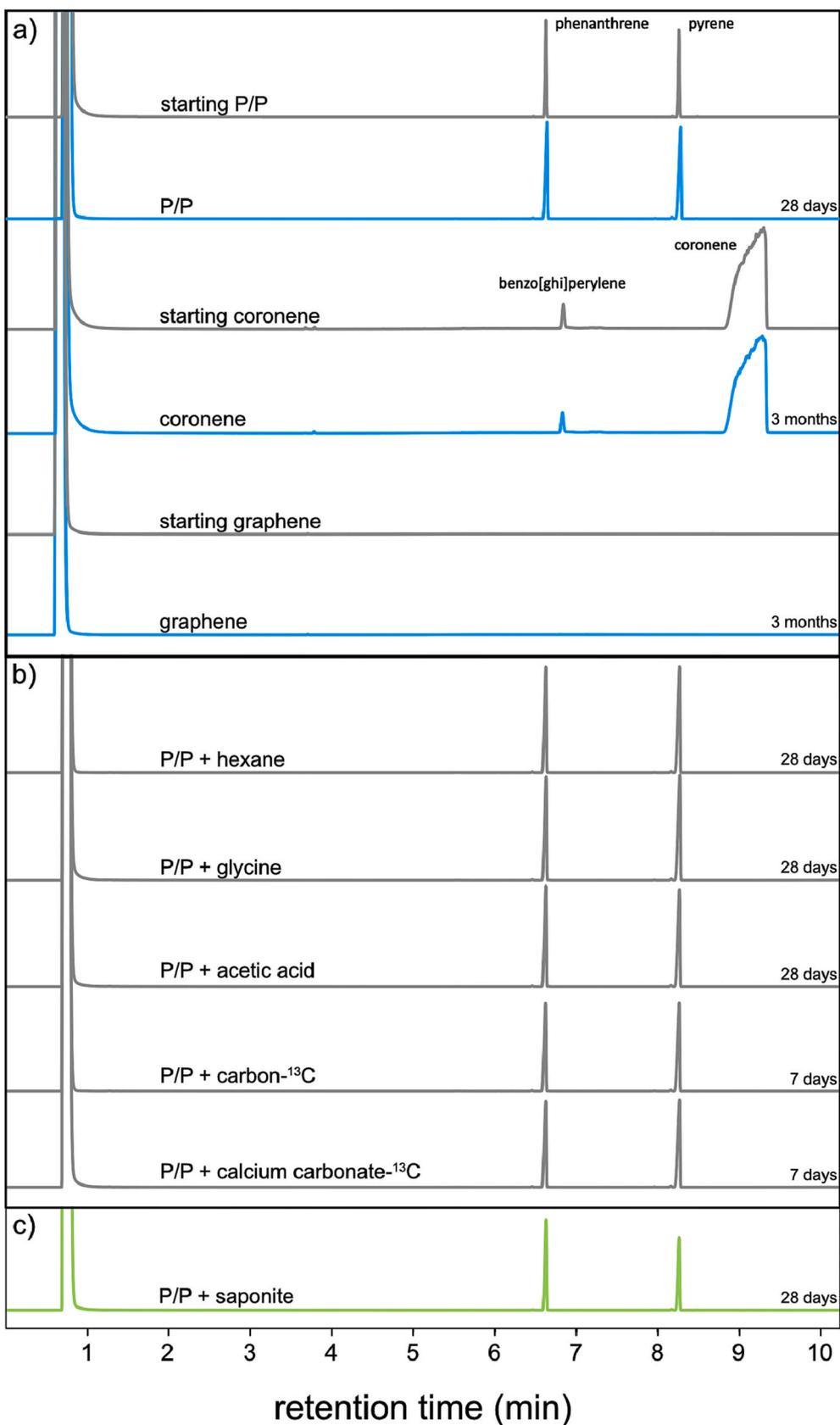
### 3.6. Experiments with saponite

We also conducted experiments with phenanthrene and pyrene at 150 °C for 28 days in the presence of saponite (Table 1). At the end of the experiment, 0.02 bar of  $\text{CO}_2$  was detected in the gas phase as revealed by GC-TCD (Fig. 1). The solvent extract of the residues of the experiments contain both pyrene and phenanthrene as revealed by GC-FID (Fig. 2), in relative amounts different from those of the starting materials: only 91.4 and 77.8% of the initial phenanthrene and pyrene compounds, respectively, were recovered in solvents at the end of the experiments (Fig. 4). Of note, the solid residues of the experiments contain about 1.4 wt% of organic carbon, which correspond to about 80% of the missing carbon (12.28 mg vs 15.40 mg) in the soluble fraction. As a fraction of saponite (3.2%) has been lost (871.2 mg of residual saponite instead of 900 mg initially), either due to dissolution or during the extraction process and sampling process, this may explain in part the missing C (Fig. 4).

## 4. Discussion

### 4.1. Influence of hydrothermal conditions on the molecular structure of PAHs

The presence, in CCs, of PAHs inherited from the ISM remains a subject of debate, in particular because sizes do not match: the PAHs in CCs have a lower molecular weight than their interstellar counterparts. To explain this discrepancy, some authors have invoked the effect of aqueous alteration which may break down large PAHs leading to the production of smaller ones and other molecules such as carboxylic and amino acids (Shock and Schulte, 1990). However, neither the degradation of the PAHs nor the production of other hydrocarbons occurred in the present experiments, whatever the size of the PAHs used as starting materials (including graphene which can be seen as a model for ISM-like PAHs). Moreover, we show that phenanthrene, pyrene and coronene can withstand hydrothermal asteroidal conditions (i.e. 150 °C). As shown by the experiments conducted with graphene, high molecular weight PAHs like those detected in the ISM likely withstand asteroidal conditions as well, especially as they are more refractory than lower molecular weight PAHs (Pendleton and Allamandola, 2002). The diversity in low molecular weight PAHs in CCs is thus likely not a consequence of the alteration conditions experienced by asteroids. These PAHs have rather been



**Fig. 2.** GC-FID chromatograms of solvent extracts after a) experiment with phenanthrene and pyrene, coronene and graphene, b) experiments with other materials and c) experiments with saponite. No molecular evolution is observed in our experimental conditions.

**Table 2**

Carbon isotope composition in  $\delta^{13}\text{C}_{\text{PDB}}$  ‰ for phenanthrene and pyrene after experiments at 150 °C during 7 days with glycine- $^{13}\text{C}_2$ , carbon- $^{13}\text{C}$  and calcium carbonate- $^{13}\text{C}$ . Uncertainties correspond to standard deviations on session standards. (x):number of replicates.

	Starting P/P	P/P + glycine- $^{13}\text{C}_2$	P/P + carbon- $^{13}\text{C}$	P/P + calcium carbonate- $^{13}\text{C}$
	$\delta^{13}\text{C}_{\text{PDB}}$ ‰	$\delta^{13}\text{C}_{\text{PDB}}$ ‰	$\delta^{13}\text{C}_{\text{PDB}}$ ‰	$\delta^{13}\text{C}_{\text{PDB}}$ ‰
Phenanthrene	-25.35 ± 0.17 (24)	-25.55 ± 0.25 (4)	-25.46 ± 0.17 (6)	-25.49 ± 0.17 (6)
Pyrene	-25.03 ± 0.09 (24)	-24.89 ± 0.08 (4)	-24.96 ± 0.09 (6)	-24.98 ± 0.09 (6)

accreted as is, implying that they are likely present in the ISM or in the protosolar nebula.

No PAHs larger than coronene have been found in CCs with laser desorption mass spectrometry, a more suitable method for large PAHs compared to soluble extraction and gas chromatography (Sabbah et al., 2017, 2022), even though they are detected in the ISM. Thus, either large PAHs have somehow been destroyed or have simply not been accreted onto asteroids. Oxidative photochemistry in the protosolar disk could have been responsible for the destruction of PAHs (Lee et al., 2010; Anderson et al., 2017), the fast accretion of low molecular weight PAHs having preserved them from destruction. In fact, it has been suggested that their accretion could have been faster than their destruction, compared to what have occurred for larger PAHs (Derenne et al., 2005). In contrast to large PAHs, small PAHs could have thus been condensed on ice or silicate grains and then accreted to form parent bodies and stored in solids (Derenne et al., 2005; Michoulier et al., 2018).

The relative abundance of alkylated versus non alkylated PAHs has been shown to be correlated to the extent of aqueous alteration (Elsila et al., 2005; Lecasble et al., 2022). Rather than a production of alkylated PAHs from non-alkylated PAHs during aqueous alteration, it has been suggested that non-alkylated PAHs are preferentially lost during fluid circulation as a result of a selective chromatographic separation, non-alkylated PAHs being more water soluble than their alkylated counterparts (Hahn et al., 1988; Wing and Bada, 1991a, 1991b; Elsilá et al., 2005). Strengthening this hypothesis, the laboratory experiments conducted in the present study showed that alkylation of PAHs does not occur under asteroidal conditions (i.e. 150 °C), even in the presence of reactive and small organic molecules. However, if both alkylated and non-alkylated PAHs were accreted onto asteroids, alkylated PAHs should be detected in all the CCs. But this is apparently not the case in the Paris meteorite (Martins et al., 2015), even though it has experienced weaker alteration compared to other CMs. Plus, if non-alkylated

PAHs are lost via chromatographic separation, the total abundance of PAHs should be correlated with the degree of alteration for series of CCs originating from the same parent body. But this is apparently not the case neither (Pering and Ponnampuruma, 1971; Martins et al., 2015; Lecasble et al., 2022). An explanation for this paradox may reside in the brecciated nature of most CCs (Lentfort et al., 2021), each fragment having potentially experienced an individual history.

#### 4.2. Influence of hydrothermal conditions on the isotope composition of PAHs

The production of PAHs in the ISM involves carbon addition and cyclization processes (Tielens and Charnley, 1997), leading to C-isotope

**Table 3**

Deuterium abundance as D/(D + H) for phenanthrene and pyrene after experiments at 150 °C during 7 days with D<sub>2</sub>O. Uncertainties correspond to standard deviations on session standards and on samples. (x): number of replicates.

	Starting P/P	D <sub>2</sub> O
	D/(D + H)	D/(D + H)
Phenanthrene	1.38 ± 0.78 × 10 <sup>-4</sup> (6)	5.89 ± 0.57 × 10 <sup>-3</sup> (4)
Pyrene	1.39 ± 0.78 × 10 <sup>-4</sup> (6)	1.02 ± 0.23 × 10 <sup>-2</sup> (4)

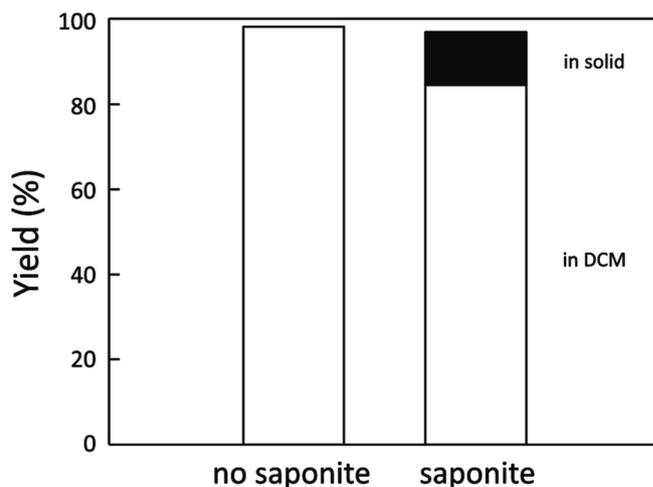


Fig. 4. Comparison of the yield of the experiment with and without saponite. PAHs are recovered in the soluble fraction (white) or in the solid phase (black).

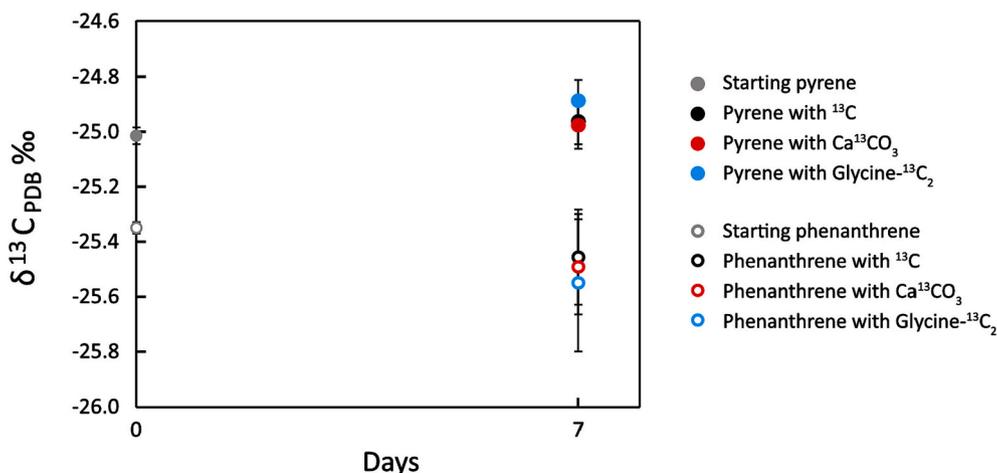


Fig. 3. Carbon isotope values of phenanthrene and pyrene before and after 150 °C alteration experiments in the presence of pure  $^{13}\text{C}$  materials. No carbon isotope exchange is observed. Error bars represent standard deviations.

compositions defining a negative trend with increasing PAH size (Gilmour and Pillinger, 1994; Naraoka et al., 2000). The similar trend observed for PAHs in CCs have led authors to suggest that PAHs found in CCs were produced in the ISM (Sephton et al., 1998; Gilmour and Pillinger, 1994; Naraoka et al., 2000; Huang et al., 2015; Lecasble et al., 2022). Strengthening this hypothesis, the laboratory experiments conducted in the present study showed that the carbon isotope composition of PAHs does not change under asteroidal conditions (i.e. 150 °C), even in the presence of other carbon reservoirs, either organic or inorganic. This is consistent with individual PAHs having quite the same carbon isotope signature in different CCs (Sephton et al., 1998; Gilmour and Pillinger, 1994; Naraoka et al., 2000; Huang et al., 2015; Lecasble et al., 2022). However, small variations remain: the same PAHs do not exhibit the exact same carbon isotope compositions in different CCs. This suggests either that the carbon isotopic composition of PAHs may slightly change after their production under conditions not simulated here, or that some of the PAHs have been produced via other pathways, possibly including the destruction of larger PAHs.

Results are different for the hydrogen isotope compositions. The PAHs produced in the ISM are expected to be deuterium-rich (Allamandola et al., 1989; Tielens and Charnley, 1997; Millar et al., 2000; Peeters et al., 2004; Salama, 2008) while the PAHs found in CCs contain less deuterium than most of the organic components investigated to far, like amino acids and IOM (Oba and Naraoka, 2003; Elsilä et al., 2012; Huang et al., 2015; Lecasble et al., 2022; Graham et al., 2022). A cause of this discrepancy could be the effect of aqueous alteration on the parent body. Strengthening this hypothesis, Oba and Naraoka (2003) showed that hydrogen isotope composition of PAHs could evolve under acidic conditions (pH = 2). The present study demonstrates that D-exchange with water can occur in less acidic conditions (starting water pH between 4 and 5) at temperatures typical of asteroidal alteration (i.e. 150 °C). A recent study has reported that the water which circulated onto the CM parent body was D-poor (Piani et al., 2021), which would explain why the PAHs found in CMs are poor in D despite a possible interstellar origin (Lecasble et al., 2022). However, a large range of  $\delta D$  values has been reported in the literature for PAHs in CCs, from very negative values (Oba and Naraoka, 2003; Graham et al., 2022; Lecasble et al., 2022) to very positive values (Huang et al., 2015; Graham et al., 2022). For instance, the  $\delta D$  value of pyrene extracted from Murchison varies by  $>750$  ‰ among different studies (Oba and Naraoka, 2003; Huang et al., 2015; Graham et al., 2022), highlighting the need for more data to accurately interpret the hydrogen isotope compositions of PAHs in CCs. In addition, the present experiments showed that the extent of isotope exchange varies with the size of the PAH, pyrene getting more D-rich than phenanthrene after 7 days in  $D_2O$  at 150 °C. Although this would need confirmation, such a result sheds new light on the negative correlation between the sizes and the  $\delta D$  values of PAHs in CCs recently reported by Graham et al. (2022). These authors interpreted this anti-correlation as resulting from preferential enrichment of low molecular weight gas-phase PAHs by unimolecular photodissociation before accretion. Alternatively, as shown here, this anti-correlation may result from hydrogen isotope exchange between PAHs and water during aqueous alteration onto asteroids.

### 4.3. Influence of the presence of clay minerals

Phyllosilicates are major constituents of carbonaceous chondrites (Pearson et al., 2006; Garvie and Buseck, 2007) and may significantly influence organic reactions (Vinogradoff et al., 2020a, 2020b; Viennet et al., 2022). However, their possible role on the molecular evolution of PAHs under hydrothermal conditions has only been understudied. Watson and Sephton (2015) showed that Fe-rich montmorillonite could enhance PAH polymerization in a dry environment at temperatures typical of that experienced by CCs. But Fe-rich montmorillonites have only been detected in CAIs of some CV chondrites (Tomeoka and Buseck, 1982), the phyllosilicates in CIs and CMs mostly being Fe–Mg

serpentes and Mg-smectites (i.e. saponites) (Brearley, 2006 and reference therein). The laboratory experiments conducted here show that the presence of saponite does not lead to the production of new PAHs, confirming the experimental results of Giese et al. (2019) using serpentine produced via the alteration of olivine.

However, a significant fraction of PAHs is not recovered at the end of the experiments reported here. Most of the missing organic C seems to be trapped within the solid residues which contain about 1.4 wt% of organic carbon. These organics, whatever their nature, may either be adsorbed onto saponites or trapped within their interlayer spaces as previously reported by other experimental studies (Viennet et al., 2019, 2022). Ca-saturated smectites have the greatest adsorption capacities (Hundal et al., 2001) and many sorption mechanisms between PAHs and smectite have been proposed. These are hydrogen bonding between PAH and the water film which surrounds smectite (Schwarzenbach et al., 2003), hydrogen bonding between PAHs and intermediate polarity mineral surface domains like silanols or aluminols (Hundal et al., 2001; Lambert, 2018), noncovalent interaction between the positively charged smectite and the  $\pi$  electrons of the PAH (Ma and Dougherty, 1997; Mader et al., 1997) and capillary condensation of PAHs into nano and micropores of a smectite platelet quasicrystal network (Hundal et al., 2001; Müller et al., 2007). According to Hundal et al. (2001) and Müller et al. (2007) the latter mechanism is the more efficient to sorb PAHs on smectites.

In this study, we did not use saponification methods as they are generally not used to extract PAHs from chondrites. However, whether these trapped organics are PAHs or products of their degradation, as it would be the case with reactive organics (Viennet et al., 2019, 2022; Vinogradoff et al., 2020a, 2020b), such trapping of organic C by phyllosilicates may have biased the reported abundances of PAHs in CCs (Pering and Ponnampuruma, 1971; Martins et al., 2015; Lecasble et al., 2022), even if more efficient extraction methods were used. Here, more pyrene than phenanthrene is missing in the soluble fraction at the end of the experiment (only 77.8% of the initial pyrene was recovered versus 91.4% of the initial phenanthrene), suggesting that smectites may trap large PAHs more efficiently. Extrapolating this result to large PAHs similar to those detected in the ISM, trapping by phyllosilicates may be invoked to explain their apparent absence in CCs.

More generally, the capabilities of smectites to trap organics, thereby hampering their extraction (Viennet et al., 2022), may account for the missing organic C paradox of CCs. Indeed, there is a difference between TOC values and the sum of the IOM and SOM contents of most CIs and CMs (Pearson et al., 2006; Alexander et al., 2015). This missing organic C could consist in large PAHs similar to those detected in the ISM, impossible to extract using solvents, but lost during acid leaching hence not recovered within the IOM. In any case, the present experimental results show that PAHs of CCs can be used as tracers of both pre-accretion and secondary processes. This work also pleads for additional experiments in the presence of phyllosilicates to further explore their influence on the signals carried by organic compounds in CCs.

### 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.

### Data availability

Data will be made available on request.

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