



Hydrogen and carbon isotopic ratios of polycyclic aromatic compounds in two CM2 carbonaceous chondrites and implications for prebiotic organic synthesis



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ABSTRACT

Study of meteoritic organic compounds offers a unique opportunity to understand the origins of the organic matter in the early Solar System. Meteoritic polycyclic aromatic hydrocarbons (PAHs) and heteropolycyclic aromatic compounds (HACs) have been studied for over fifty years, however; their hydrogen stable isotopic ratios (δD) have never been reported. Compound-specific δD measurements of PAHs and HACs are important, in part because the carbon isotopic ratios ($\delta^{13}C$) of various meteoritic PAHs cannot be readily distinguished from their terrestrial counterparts and it is difficult to rule out terrestrial contamination based on carbon isotopic ratios alone. In this study, we have extracted and identified more than sixty PAHs and HACs present in two CM2 carbonaceous chondrites Murchison and LON 94101. Their carbon and hydrogen stable isotopic ratios ($\delta^{13}C$ and δD) were measured and used to discuss about their synthetic environments and formation mechanisms. The concentration of aromatic compounds is $\sim 30\%$ higher in Murchison than in the Antarctic meteorite LON 94101, but both samples contained similar suites of PAHs and HACs. All PAHs and HACs found exhibited positive δD values (up to 1100%) consistent with an extraterrestrial origin, indicating the relatively low $\delta^{13}C$ values are indeed an inherent feature of the meteoritic aromatic compounds. The hydrogen isotopic data suggest aromatic compounds in carbonaceous chondrites were mainly formed in the cold interstellar environments. Molecular level variations in hydrogen and carbon isotopic values offer new insights to the formation pathways for the aromatic compounds in carbonaceous chondrites.

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1. Introduction

Carbonaceous chondrites are among the most primitive materials in the Solar System. This type of meteorites can contain up to 14 wt% of water and 5 wt% of organic carbon that survived planet formation processes by being incorporated into an asteroid parent body (Cronin and Chang, 1993; Sephton, 2002). In CM2 carbonaceous chondrites, up to 30% of the total amount of organic material can be in the form of solvent-soluble compounds (Pizzarello et al., 2006), with the rest being macromolecular organic matter rich in polynuclear aromatic structures linked by aliphatic moieties (Cody and Alexander, 2005; Remusat et al., 2005; Huang et al., 2007). Polycyclic aromatic hydrocarbons (PAHs) are some of the most ubiquitous organic compounds found in the universe, and have been detected in interplanetary dust par-

ticles, the interstellar medium (ISM) and asteroidal meteorite parent bodies (e.g., Allamandola et al., 1987; Clemett et al., 1993; Basile et al., 1984). PAHs and HACs may serve as membrane stabilizers for primitive cells on the prebiotic Earth and have special astrobiological significance (Groen et al., 2012). However, these molecules are also abundant in organic materials formed on Earth through natural and anthropogenic combustion processes (e.g., Denis et al., 2012 and references therein). The potential complex sources for PAHs place their primordial origin in carbonaceous chondrites under debate.

The analysis of aromatic hydrocarbons in carbonaceous chondrites using liquid chromatography and spectrophotometric methods date back to the early 1960s, when compounds such as phenanthrenes and pyrenes were identified from aromatic hydrocarbon fractions of Orgueil, Murray, Cold Bokkeveld and Allende meteorites (Studier et al., 1972; Commins and Harington, 1966). However; because of the complex origins for PAHs, without pristine samples or obtaining isotopic information, it was difficult to exclude terrestrial contamination as the sources of PAHs and HACs

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in carbonaceous chondrites. Shortly after its fall in 1969, studies of Murchison, an observed fall, greatly strengthened the notion that PAHs might be indigenous in carbonaceous meteorites (Oró et al., 1971; Kvenvolden et al., 1970; Pering and Ponnampetuma, 1971; Studier et al., 1972; Basile et al., 1984). One long standing, puzzling observation, however, is that the carbon isotopic ($\delta^{13}\text{C}$) values of PAHs such as benzene, toluene, naphthalene, biphenyl, phenanthrene and pyrenes in Murchison display significant overlap with those of terrestrial compounds (Yuen et al., 1984; Sephton et al., 1998; Sephton and Gilmour, 2000, 2001; Naraoka et al., 2000). The situation is exacerbated by the identification of terrestrial aliphatic compounds such as isoprenoidal hydrocarbons in the Murchison carbonaceous chondrite (Hayes, 1967), making it difficult to completely rule out terrestrial contamination of PAHs in carbonaceous chondrites.

Hydrogen isotopic ratios (δD) of PAHs in carbonaceous chondrites have not previously been reported, probably because these compounds contain significantly fewer hydrogen atoms per molecule, making the measurement of the compound specific hydrogen isotopic ratios using GC-IRMS more challenging than aliphatic compounds. The only previous attempt to determine hydrogen isotopic ratios of aromatic hydrocarbons was to measure bulk fractions from chromatographic separations (Krishnamurthy et al., 1992). However, these bulk fractions may contain various kinds of unidentified compounds (hence the resulting isotopic data cannot be attributed specifically to PAHs). Compound specific δD values of PAHs could provide more definitive evidence for the extraterrestrial origins and synthetic environments of these meteoritic organic compounds than carbon isotopic values, as exemplified by more polar compounds such as amino acids (Epstein et al., 1987; Pizzarello et al., 1991; Pizzarello and Huang, 2005; Elsilá et al., 2012), and carboxylic acids (Huang et al., 2005, 2007; Aponte et al., 2011, 2014), which are highly enriched in D relatively to their terrestrial counterparts, indicating they originated in cold interstellar environments.

The objectives of this study are two folds: 1) to determine the hydrogen isotopic ratios of individual PAHs (and in cases of partial chromatographic coelution, combined hydrogen isotopic values of multiple PAHs or HACs) in two CM2 carbonaceous chondrites (Murchison and LON94101) and use the data to infer PAH origins and synthetic pathways; 2) to compare the carbon and hydrogen isotopic differences among PAHs and HACs to probe into their synthetic mechanisms. Our study fills an important gap in the analysis of PAHs from the solvent soluble fraction of carbonaceous chondrites, since the δD values for meteoritic PAHs and HACs have not been reported before.

2. Methods and materials

2.1. Meteorite extraction

PAHs are ubiquitously present on the Earth biosphere, hence the possibility of terrestrial contamination of meteorite samples is not trivial. To best differentiate indigenous PAHs and other organic compounds from possible contaminants, we also analyzed Lonewolf Nunataks (LON) 94101 (an Antarctic meteorite) in addition to Murchison (Aponte et al., 2014). LON 94101.59 (5.17 g) were obtained from the Antarctic Meteorite Collection (NASA), and Murchison (catalog number: USNM 6650; CM2; 4.68 g) from the Smithsonian Institution. Both belong to CM2 carbonaceous chondrites that experienced substantial aqueous alteration. However, LON 94101 belongs to subtype CM2.2–2.3, which experienced greater extent of aqueous alteration than Murchison (CM2.5) (Lee et al., 2014). The meteorites' outer-most layers were removed with a solvent-cleaned metal file at Brown University. The remaining inner samples were powdered on a clean agate mortar

and suspended in 10 mL of an aqueous 1N NaOH solution. Upon sonication for 30 min and stirring for 2 h at room temperature, the suspension was centrifuged and the aqueous layer was separated and kept for previously reported analyses of monocarboxylic acids (Aponte et al., 2014). The remaining powders were extracted with methanol first (three times, 10 mL each), followed by dichloromethane (two times, 10 mL each) using ultrasonication for 30 min at 50 °C. The solvent extracts were combined and dried over anhydrous sodium sulfate. Freshly prepared copper beads (i.e., surface CuO is first removed by rinsing in 0.1M HCl, followed by water and solvent cleaning) were added to these combined solvent extracts to remove sulfur and then the total volume was reduced to 0.5 mL, and then subjected to Gas Chromatography-Flame Ionization Detector (GC-FID), GC-Mass Spectrometry (MS) and GC-Isotope Ratio Mass Spectrometer (IRMS) analysis. GCMS analyses reveal majority (>90%) of the compounds in the combined solvent extract were PAHs and HACs in both meteorite samples (Fig. 1). To minimize loss of compounds and possibility of contamination, no liquid chromatographic separation was carried out prior to compound specific isotopic analysis.

2.2. GC-MS and GC-IRMS analyses

Identification of compounds was achieved using an HP6890+ GC interfaced to 5973 N mass detector (MSD). PAHs and HACs in our samples were identified using GC-MS and by running authentic standards when even possible (compounds 6, 8, 15, 31, 32, 45, 47, 56, 57, and 60 to 64). Quantification was done by GC-MS using calibration lines of different PAHs and HACs. For those we did not have standards, we used calibration of standard compounds with the closest structures (i.e., assuming the same response factors). Compound specific isotope ratios were determined with an HP6890+ GC connected to a Finnigan MAT Delta+XL mass spectrometer. In all analyses, a DB-5MS 60 m \times 0.25 \times 0.1 μm capillary column (Agilent) was used. Helium carrier gas flow was 1.1 mL/min. The injection port was set at 320 °C. The oven temperature was programmed to rise from 60 °C (hold for 1 min) to 310 °C at 6 °C min⁻¹ (hold for 20 min). The $\delta^{13}\text{C}$ and δD values are reported relative to the Vienna Pee Dee Belemnite (VPDB) and Vienna Standard Mean Ocean Water (VSMOW) standards, respectively. For $\delta^{13}\text{C}$ isotope ratio measurements, compounds separated by GC column were converted to CO₂ and H₂O in a combustion furnace (0.5 mm ID \times 1.5 mm OD \times 34 cm) operated at 940 °C and loaded with CuO and Pt wires as oxidant and catalyst, respectively (Huang et al., 2005). A small stream of 1% O₂ in He was added right in front of the reactor to maintain the oxidation capacity of the CuO. Six pulses of CO₂ reference gas of known $\delta^{13}\text{C}$ values were injected via the interface to the IRMS, for the computation of $\delta^{13}\text{C}$ values of sample compounds. After compound identification by GC-MS and compound specific carbon isotopic analysis, hydrogen isotope analyses of PAHs were performed using a high temperature conversion reactor. The same GC system and temperature programming as for the carbon analyses were used, except for replacing the oxidation reactor with a pyrolysis reactor. Compounds separated by GC were converted to H₂ through a pyrolysis furnace operated at 1445 °C (Burgoyne and Hayes, 1998). Six pulses of hydrogen reference gas with known δD values were injected via the interface to the IRMS, for the computation of δD values of sample compounds (Huang et al., 2005; Huang et al., 2007). The accuracy of the isotopic measurements was routinely established by measuring lab standards (mixture of C₁₆, C₁₈, C₂₂, C₂₄, C₂₆ and C₂₈ fatty acid methyl esters and mixture of C₂₃, C₂₇ and C₂₉ *n*-alkanes) with known H and C isotopic values. The lab standards were established by repeated measurements (~50 times) after verifying the machine performance using the standard compounds (C₁₆, C₁₈, C₂₀ and C₃₀ *n*-alkanes acquired

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