Data Article

A dataset representing the impact of aromatic nuclei on the carbon isotope of gases

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ABSTRACT

This work presents a dataset which provides information on the influence of aromatic nuclei on the carbon isotope of gases. Gases analyzed herein were obtained by pyrolysis of model compounds and kerogens. The carbon isotope of gases from paraffin cracking with and without the addition of aromatic nuclei is summarized. We also obtained carbon isotope data for the gases from different type of kerogens, which indicate the role of aromatic nuclei in the formation of natural gases from kerogen cracking. Further interpretation and discussion of these data can be found in the related research article entitled “The methylation of aromatic nuclei — I: Implications for the geochemical evolution of gas” [1].

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1. Data description

To understand the impact of aromatic nuclei and their methylation reactions on the carbon isotope of gases, several model compounds and kerogen samples were selected and subjected to pyrolysis

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2. Experimental design, materials, and methods

2.1. Chemical and materials

Model compounds were selected to investigate the mechanism of effect of aromatic nuclei, while kerogens were selected to understand the action of aromatic nuclei in complex geological systems. Detailed information for model compounds and kerogens were described in the related research article [1]. Briefly, n-tricosane (n-C23), n-tetracosane (n-C24), naphthalene (N), and montmorillonite KSF were obtained from commercial suppliers and used as received. Four kerogen samples selected for pyrolysis experiments were prepared from the following rocks using the traditional HF–HCl approach [2]. The samples comprised the Green River formation shale from the Green River Basin (Type-I), the oil shale from the Minhe Basin (Type-II/a), the carbonaceous shale from the Yanqi Basin (Type-II/b), and the brown coal from the Huang County Basin (Type-III). Macromolecular aromatic nuclei (KEROGEN-500) were obtained by artificial maturation of the Type-II/b kerogen, which was performed in a closed system at 500 °C for 72 h to reduce its gas formation ability.
peratures were 350, 360, 370, 380, and 390 °C were used to understand the effect of aromatic nuclei under the catalysis of clay. The pyrolysis dosage for other three systems was the same as the glass tube (22-cm length, 1.3-cm internal diameter, and 0.2-cm thick). The tube was flushed with dry air five times to ensure the complete removal of air. It was then evacuated, and sealed. The tube was placed in Muffle furnace and heated at the desired temperature for a time period of 72 h at a heating rate of 2 °C/min. After cooling the tube to room temperature, it was placed in a vacuum line (pressure equal to 10^{-5} MPa). After isolating the extraction line from the vacuum pump, each tube was carefully broken into pieces to liberate the generated gases, which was pumped into a calibrated volume to quantify their total yield and recover them for molecular and isotopic analysis.

### Table 1
Carbon isotope data of the gases from the pyrolysis of the paraffin (n-C_{23}) in the different reaction systems (n-C_{23}, n-C_{23}+N, n-C_{23}+KSF, and n-C_{23}+N + KSF).

| T (°C) | δ^{13}C (%) | δ^{13}C_{2}/δ^{13}C_{1} (%) |
|--------|-------------|-----------------------------|
|        | CH_{4}      | C_{2}H_{4} | C_{2}H_{6} | C_{3}H_{8} | C_{3}H_{6} | C_{3}H_{8} |
| n-C_{23} |            |            |            |            |            |            |
| 370    | –61.7      | –29.9      | –40.7      | –25.5      | –37.2      | 21.0       |
| 390    | –55.4      | –25.3      | –38.2      | –17.1      | –35.8      | 17.2       |
| 410    | –51.9      | –24.9      | –36.1      | –15.1      | –33.6      | 15.9       |
| n-C_{23}+N |        |            |            |            |            |            |
| 370    | –59.9      | –28.4      | –40.4      | –31.0      | –37.5      | 19.5       |
| 390    | –55.4      | –25.4      | –37.7      | –21.1      | –35.8      | 17.7       |
| 410    | –51.4      | –26.0      | –35.9      | –17.7      | –34.9      | 15.4       |
| n-C_{23}+KSF |     |            |            |            |            |            |
| 350    | –50.5      | –30.4      | –41.7      | –22.0      | –40.5      | 8.6        |
| 360    | –51.8      | –32.9      | –42.2      | –18.8      | –40.3      | 9.6        |
| 370    | –52.4      | –30.5      | –42.5      | –20.8      | –40.4      | 10.0       |
| 380    | –52.2      | –29.5      | –41.7      | –18.1      | –38.9      | 10.4       |
| 390    | –50.8      | –32.1      | –41.0      | –9.9       | –38.5      | 9.8        |
| n-C_{23}+N + KSF |   |            |            |            |            |            |
| 350    | –46.3      | –29.1      | –37.4      | –19.3      | –37.6      | 8.8        |
| 360    | –49.4      | –34.0      | –39.8      | –21.7      | –38.9      | 9.6        |
| 370    | –52.1      | –31.7      | –42.3      | –19.2      | –40.4      | 9.9        |
| 380    | –53.3      | –29.9      | –41.6      | –24.0      | –40.2      | 11.7       |
| 390    | –54.1      | –27.1      | –42.1      | –17.2      | –37.9      | 12.0       |

### Table 2
Carbon isotope data of the gases from the pyrolysis of the paraffin (n-C_{24}) in the presence of macromolecular aromatic nuclei and montmorillonite (n-C_{24}+KSF + KEROGEN-500).

| T (°C) | δ^{13}C (%) | δ^{13}C_{2}/δ^{13}C_{1} (%) |
|--------|-------------|-----------------------------|
|        | CH_{4}      | C_{2}H_{6} | C_{2}H_{8} | C_{3}H_{8} | n-C_{4}H_{10} | C. |
| 340    | –42.9      | –36.7      | –34.9      | –33.6      | 6.1       |
| 360    | –46.2      | –38.0      | –36.4      | –34.6      | 8.2       |
| 380    | –47.3      | –40.1      | –37.2      | –34.3      | 7.2       |
| 400    | –47.9      | –39.4      | –35.5      | –33.0      | 8.5       |
| 420    | –47.1      | –37.0      | –30.2      | –17.0      | 10.1      |
| 440    | –46.2      | –33.0      | –24.7      | –a         | 13.3      |
| 460    | –44.4      | –30.6      | –a         | –a         | 13.9      |
| 480    | –42.3      | –26.5      | –a         | –a         | 15.8      |
| 500    | –40.9      | –21.6      | –a         | –a         | 19.3      |

a Not determined.

### 2.2. Pyrolysis experiments

1) The systems of n-C_{23}/n-C_{23}+N/n-C_{23}+KSF/n-C_{23}+N + KSF

The n-C_{23} and n-C_{23}+N systems were designed to investigate the influence of aromatic nuclei without a catalyst. They were pyrolyzed at 370, 390, and 410 °C. The n-C_{23}+KSF and n-C_{23}+N + KSF systems were used to understand the effect of aromatic nuclei under the catalysis of clay. The pyrolysis temperatures were 350, 360, 370, 380, and 390 °C. The n-C_{23}+N + KSF system was taken as an example to illustrate the experimental procedures. A mixture of n-C_{23}+N + KSF (300 mg: 150 mg: 1500 mg) (the dosage for other three systems was the same as the n-C_{23}+N + KSF system) was added to the Pyrex glass tube (22-cm length, 1.3-cm internal diameter, and 0.2-cm thick). The tube was flushed with dry nitrogen five times to ensure the complete removal of air. It was then evacuated, and sealed. The tube was placed in Muffle furnace and heated at the desired temperature for a time period of 72 h at a heating rate of 2 °C/min. After cooling the tube to room temperature, it was placed in a vacuum line (pressure equal to 10^{-5} MPa). After isolating the extraction line from the vacuum pump, each tube was carefully broken into pieces to liberate the generated gases, which was pumped into a calibrated volume to quantify their total yield and recover them for molecular and isotopic analysis.
2) The system of \( n\)-C24 + KEROGEN-500 + KSF

This system was designed to investigate the role of macromolecular aromatic nuclei with montmorillonite. A mixture of \( n\)-C24/KEROGEN -500/KSF (300 mg:150 mg:1500 mg) was added to the Pyrex glass tube. They were pyrolyzed at 340, 360, 380, 400, 420, 440, 460, 480, and 500 °C for a time period of 72 h. The experimental process was the same as described above.

3) Kerogens and the mixtures of the kerogen and montmorillonite KSF

The kerogens as well as the mixtures of the kerogen and montmorillonite KSF (ratio of 1:2, usually 500 mg of kerogen with 1000 mg of mineral) were also sealed in the Pyrex tubes under vacuum. They were pyrolyzed at a temperature of 300, 350, 400, and 450 °C. The pyrolysis experiments were performed using the same procedures described above.

2.3. \( \delta^{13} \text{C} \) measurements of gaseous products

Compound-specific isotopic analysis of gaseous products was performed on a Finnigan Mat DELTA plus isotope ratio mass spectrometer (iMS) connected to an HP 5890II gas chromatograph (GC). The GC was equipped with a split/splitless inlet system and a 30 m × 0.32 mm i.d. HP-PLOT Q column.

### Table 3
Carbon isotope data of the gases from the pyrolysis of kerogen with and without montmorillonite.

| T(°C) | \( \delta^{13} \text{C}(‰) \) | \( \delta^{13} \text{C}_2-\delta^{13} \text{C}_1(‰) \) |
|-------|-----------------|-----------------|
|       | \( \text{CH}_4 \) | \( \text{C}_2\text{H}_6 \) | \( \text{C}_3\text{H}_8 \) | \( \text{CO}_2 \) |
| TYPE-I | 300 | -48.6 | -38.5 | -35.9 | -13.6 | 10.2 |
|       | 350 | -47.7 | -37.6 | -33.6 | -11.5 | 10.1 |
|       | 400 | -47.1 | -39.0 | -36.5 | -12.1 | 8.1 |
|       | 450 | -43.4 | -35.3 | -27.5 | -14.0 | 8.1 |
| TYPE-I+KSF | 300 | -48.5 | -38.3 | -36.0 | -13.4 | 10.3 |
|       | 350 | -47.8 | -37.3 | -33.6 | -14.2 | 10.6 |
|       | 400 | -44.8 | -37.3 | -34.9 | -14.7 | 7.5 |
|       | 450 | -42.2 | -35.0 | -26.6 | -15.0 | 7.2 |
| TYPE-II/a | 300 | -33.4 | -31.7 | -31.4 | -12.6 | 1.7 |
|       | 350 | -36.2 | -32.2 | -26.6 | -14.0 | 4.0 |
|       | 400 | -34.2 | -28.3 | -25.8 | -14.3 | 5.9 |
|       | 450 | -31.0 | -26.3 | -14.6 | -14.1 | 4.7 |
| TYPE-II/a+KSF | 300 | -32.9 | -29.2 | -28.7 | -13.6 | 3.7 |
|       | 350 | -36.5 | -29.3 | -23.6 | -15.2 | 7.2 |
|       | 400 | -34.0 | -27.7 | -23.8 | -15.6 | 6.3 |
|       | 450 | -31.4 | -20.5 | -19.2 | -16.8 | 10.9 |
| TYPE-II/b | 300 | -39.7 | -33.4 | -31.0 | -12.7 | 6.3 |
|       | 350 | -42.3 | -33.2 | -27.8 | -14.0 | 9.1 |
|       | 400 | -38.2 | -30.7 | -27.6 | -14.0 | 7.5 |
|       | 450 | -33.8 | -27.7 | -16.0 | -15.1 | 6.1 |
| TYPE-II/b+KSF | 300 | -38.6 | -32.6 | -29.7 | -14.6 | 6.1 |
|       | 350 | -40.0 | -31.5 | -26.8 | -16.6 | 8.4 |
|       | 400 | -36.6 | -29.1 | -24.1 | -15.3 | 7.5 |
|       | 450 | -32.8 | -20.1 | -23.5 | -17.1 | 12.7 |
| TYPE-III | 300 | -34.2 | -28.4 | -26.5 | -13.2 | 5.7 |
|       | 350 | -35.6 | -27.2 | -25.1 | -12.5 | 8.4 |
|       | 400 | -33.4 | -27.3 | -24.8 | -14.0 | 6.1 |
|       | 450 | -28.4 | -22.5 | -3 | -14.5 | 5.9 |
| TYPE-III+KSF | 300 | -33.4 | -27.7 | -25.1 | -15.6 | 5.7 |
|       | 350 | -34.2 | -26.4 | -23.5 | -16.3 | 7.8 |
|       | 400 | -34.1 | -26.0 | -22.4 | -16.0 | 8.0 |
|       | 450 | -29.7 | -18.7 | - | -16.8 | 11.0 |

\(^a\) Not determined.
(film thickness 0.25 μm; Agilent, USA). The GC oven temperature was increased from 60 °C to 200 °C at 8 °C/min with initial and final hold times of 5 and 20 min, respectively. The separated compounds were converted to CO₂ by passing the eluting analyte stream through a ceramic oxidation reactor (with three braided NiO/CuO/Pt wires) at a temperature of 930 °C. The $^{13}$C of CH₄ reference gas was monitored for every three samples to ensure that the precision and accuracy of the determination were maintained. The measurement precision was ±0.5‰ for δ¹³C.

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Conflict of 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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