# Research Article

# Carbon isotope analyses of *n*-alkanes released from rapid pyrolysis of oil asphaltenes in a closed system

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**RATIONALE:** Carbon isotope analysis of *n*-alkanes produced by the pyrolysis of oil asphaltenes is a useful tool for characterizing and correlating oil sources. Low-temperature (320–350°C) pyrolysis lasting 2–3 days is usually employed in such studies. Establishing a rapid pyrolysis method is necessary to reduce the time taken for the pretreatment process in isotope analyses.

**METHODS:** One asphaltene sample was pyrolyzed in sealed ampoules for different durations (60–120 s) at 610°C. The $\delta^{13}$C values of the pyrolysates were determined by gas chromatography/combustion/isotope ratio mass spectrometry (GC/C/IRMS). The molecular characteristics and isotopic signatures of the pyrolysates were investigated for the different pyrolysis durations and compared with results obtained using the normal pyrolysis method, to determine the optimum time interval. Several asphaltene samples derived from various sources were analyzed using this method.

**RESULTS:** The asphaltene pyrolysates of each sample were similar to those obtained by the flash pyrolysis method on similar samples. However, the molecular characteristics of the pyrolysates obtained over durations longer than 90 s showed intensified secondary reactions. The carbon isotopic signatures of individual compounds obtained at pyrolysis durations less than 90 s were consistent with those obtained from typical low-temperature pyrolysis. Several asphaltene samples from various sources released *n*-alkanes with distinct carbon isotopic signatures.

**CONCLUSIONS:** This easy-to-use pyrolysis method, combined with a subsequent purification procedure, can be used to rapidly obtain clean *n*-alkanes from oil asphaltenes. Carbon isotopic signatures of *n*-alkanes released from oil asphaltenes from different sources demonstrate the potential application of this method in 'oil–oil' and 'oil–source' correlations. Copyright © 2016 John Wiley & Sons, Ltd.

Asphaltenes in oil are defined by their solubility as the macromolecular aggregates that are insoluble in low-boiling-point alkanes (usually $C_5$–$C_7$).[1,2] Previous pyrolysis studies have shown that: (1) oil asphaltenes are formed at the early stage of kerogen cracking and bear structural similarities to their source kerogen;[1–3] (2) even in the case of oil that has lost almost all of the hydrocarbons by severe biodegradation, oil asphaltenes release abundant products upon pyrolysis that are similar in composition to undegraded oils;[4,5] (3) asphaltene molecules released by pyrolysis are only slightly affected by oil migration or precipitation.[6,7] Therefore, compound-specific carbon isotope analyses of pyrolysis products (mainly *n*-alkanes) of oil asphaltenes are usually used to characterize oil sources, perform oil–oil correlations and evaluate oil mixing.[8–15]

Pyrolyses of asphaltenes for carbon isotope analyses have mostly been conducted in closed systems for 2–3 days at relatively low temperatures (320–350°C).[8–10,12–15] Carbon isotope analysis usually requires a low background and

excellent separation of individual compounds. The oil or pyrolysis products of asphaltenes are complex mixtures of molecules of different masses and structures. Hence, preliminary separation by column chromatography and subsequent purification by size-exclusion methods (e.g., urea adduction or molecular sieving) are preferred for obtaining a clean *n*-alkane fraction from the pyrolysates or oil in most studies.[12–16] As a result, asphaltene pyrolysis and subsequent purification procedures normally take several days to complete prior to using isotope ratio mass spectrometry (IRMS) to carry out carbon isotope analyses.

In this work, a series of pyrolysis experiments was performed on an oil asphaltene sample in sealed glass ampoules at a much higher temperature (610°C) than is normally applied,[12–15] to develop a rapid method of obtaining the carbon isotopic ratios of *n*-alkanes for correlation studies. The effects of pyrolysis durations were investigated, in terms of the molecular characteristics of the pyrolysates and on the carbon isotopic signatures of the released *n*-alkanes. These were compared with the molecular and isotopic characteristics reported for the same sample using the normal pyrolysis method.[13] Several oil asphaltenes from a variety of sources were further analyzed using this procedure to validate its ability to identify source-related differences in carbon isotopic signatures.

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## EXPERIMENTAL

### Samples

Five of the asphaltene samples characterized by pyrolysis in our previous studies were selected for comparison (Table 1).[13,14] One sample (HD11C) was used to investigate the effect of pyrolysis duration. These asphaltenes were extracted from oil or tar sands originating in the Cambrian–Ordovician marine source rocks in the Tarim Basin, northwest China.[13,14,17] Two asphaltene samples (TD2, TZ62S) which showed enrichment in $^{13}C$ (Table 1) were also separated from marine oil from the Tarim Basin in this study. The carbon and hydrogen isotope ratios of the n-alkanes in these samples indicate a distinct origin from most marine oil in the basin.[17]

In addition to asphaltenes from the Tarim Basin, two asphaltene samples (W580D, Wx133) were separated from oil in the Bohai Bay Basin, east China, which were sourced from Eocene Shahejie (Es) and Kongdian ($E_k$) mudrocks deposited in a lacustrine environment.[18]

### Pyrolysis experiments

A temperature of 610°C, normally applied in flash pyrolysis, was used for the rapid pyrolysis in this study. Typically, a glass ampoule ($\approx$ 5 mL) was loaded with 8–10 mg of the asphaltene sample and sealed under vacuum. The ampoule was quickly inserted into the middle section of a purpose-built tubular furnace (38 × 2.4 cm i.d.) which had been heated to 610 ± 10°C. After a short period (30, 45, 60, 75, 90, 105 and 120 s), the ampoule was removed from the furnace and cooled in ambient conditions. Sample HD11C was pyrolyzed three times for all the time intervals. The other samples were each pyrolyzed for 75 s once only.

### Separation and purification of pyrolysates

About 1 mL of n-hexane was quickly added into the opened ampoule to flush out the pyrolysates, and the extracts were filtered, and separated into saturated and aromatic fractions using microcolumn chromatography (0.6 cm i.d.) on silica gel (5 cm filling length) with n-hexane and n-hexane/dichloromethane (3:2, v/v) as the eluents. The saturated

**Table 1.** Asphaltene samples and their geological information

| Sample | Depth (m) | Type | $\delta^{13}C_{asp}$ | Source facies |
|---|---|---|---|---|
| HD11C | 5125–5128 | oil | −33.1 | Marine |
| YM2O | 5940–5943 | oil | −33.7 | Marine |
| LN2-22 T | – | oil | −33.0 | Marine |
| YW2S | 5211.2 | tar sand | −32.9 | Marine |
| TZ16C | 3812–3819 | oil | −32.4 | Marine |
| TD2 | 4561–5040 | oil | −27.0 | Marine |
| TZ62S | 4052.9–4073.6 | oil | −28.3 | Marine |
| W580D | 3167.8–3177.8 | oil | −26.4 | Lacustrine |
| Wx133 | 3179.4–3185.8 | oil | −28.9 | Lacustrine |

$\delta^{13}C_{asp}$ refers to the $\delta^{13}C$ values of asphaltenes in ‰.
Data for samples HD11C–TZ16C reported in our previous studies;[13,14] others were obtained in the present study.

fraction was purified by a 5 Å molecular sieve as described in the previously reported procedure to remove all branched alkanes and most alkenes.[19] The n-alkane fraction obtained in this way was further purified using an $AgNO_3$–silica gel column to remove the few residual alkenes.

### Gas chromatography/mass spectrometry (GC/MS) analyses

The pyrolysates were analyzed using a Thermo DSQ II single quadrupole mass spectrometer (Thermo Scientific, Austin, TX, USA) operated in electron ionization (EI) mode, interfaced with a Trace Ultra gas chromatograph (Thermo). A 30 m DB-5 ms capillary column (0.32 mm i.d., 0.25 μm film thickness; J&W Scientific, CA, USA) was used to separate the compounds being studied.

### Carbon isotope analyses

The carbon isotopic ratios of the purified n-alkane fraction were measured using a IsoPrime isotope ratio mass spectrometer (GV Instruments, Manchester, UK) connected to a HP 6890 gas chromatograph ( Agilent Technologies, Santa Clara, CA, USA) via a combustion interface. The gas chromatograph was equipped with a 30 m DB-5 ms capillary column (0.32 mm i.d., 0.25 μm film thickness; J&W Scientific, Folsom) for compound separation. A standard mixture of n-alkanes (from A. Schimmelmann, Indiana University, Bloomington, IN, USA) was measured twice daily to assess the accuracy and precision of the GC/C/IRMS analyses. The precision of the carbon isotope analyses was better than 0.3 ‰ (working standard analyses, SD = 1σ), and all the results are reported as δ values in ‰ relative to VPDB.

## RESULTS AND DISCUSSION

### Molecular characteristics of asphaltene products

Negligible amounts of pyrolysate were obtained from asphaltene HD11C after pyrolysis for 30 s and 45 s. Accordingly, only the results for 60–120 s are shown in Fig. 1. The pyrolysates obtained for different pyrolysis durations were generally similar. The most abundant components were the series of n-alk-1-ene and n-alkane doublets, which suggests a dominance of n-alkyl side chains or n-alkyl bridges bound to the condensed aromatic units of the asphaltene. This feature has previously been revealed in the pyrolysis or chemical degradation products of asphaltenes from various sources.[2,3,20] Another notable compound detected was 1,2,3,4-tetramethylbenzene (TTMB), which appears in the pyrolysates of asphaltenes from the Tarim Basin. Carbon isotope evidence indicates a major contribution from green sulfur bacteria *Chlorobiaceae*.[13,14] Other compounds detected include iso-alkane/alkenes and aromatic hydrocarbons with different ring numbers.

All the pyrolysis products obtained following our method displayed similar characteristics to those obtained by flash pyrolysis on the same sample in a previous study.[13] Flash pyrolysis features relatively high temperature (normally at 610°C), very short heating duration (a few seconds) and an open system, and is one of the most commonly used methods to investigate macromolecular characteristics. Complete series of n-alk-1-ene and n-alkane doublets are generally the
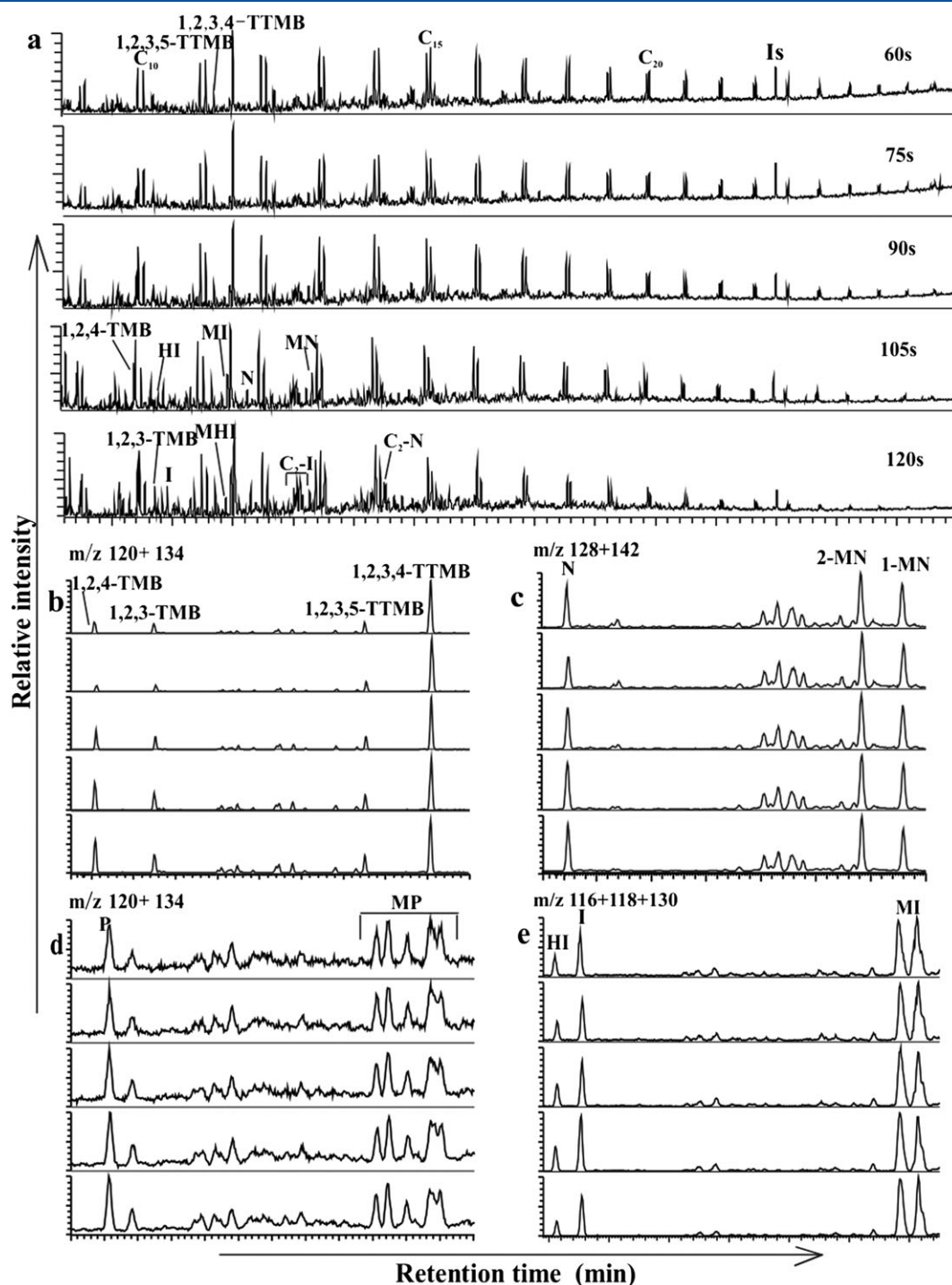
**Figure 1.** (a) Total ion current (TIC) chromatograms and (b–e) summed mass chromatograms of the pyrolysates of asphaltene HD11C at different pyrolysis durations. [$C_n$ = carbon number of the *n*-alk-1-ene and *n*-alkane doublets; Is = internal standard ($C_{24}$ deuterated *n*-alkane); TMB = trimethylbenzene; N, MN, $C_2$-N, P, MP = naphthalene, methyl naphthalene, dimethyl naphthalene, phenanthrene, methyl phenanthrene; I, MI, $C_2$-I, HI, MHI = indene, methyl indene, dimethyl indene, indane, methyl indane.]

most notable products of oil asphaltenes using this technique.[2,3,13,14] The pyrolysis of oil asphaltenes in an open system utilizing programmed-temperature heating yielded similar products.[11,21] However, programmed-temperature pyrolysis of kerogens in a closed system yielded abundant *n*-alkanes by the use of medium temperatures (420–440°C)

for about 20 min.[22] At temperatures above 500°C, secondary cracking and aromatization reactions produced a significant amount of aromatic hydrocarbons and a relatively low amount of alkanes. Low-temperature pyrolysis of oil asphaltenes over periods of a few days in a closed system produced *n*-alkane series.[4,5,8–10]

For the above reasons, a pyrolysis procedure similar to open-system high-temperature pyrolysis was used in this study. The characteristics of the pyrolysates are probably related to the short heating duration, which hinders the hydrogenation of *n*-alkenes from the free radical reactions initiated by bond breaking.

### Variations in molecular characteristics of asphaltene pyrolysates with pyrolysis duration

#### *n*-Alkene/alkanes

Due to evaporation losses during sample extraction, filtration and concentration, only $C_{14+}$ *n*-alkene/alkanes were quantified using the added internal standard (partly shown in Fig. 2). Generally, the yield of *n*-alkene/alkane doublets decreased with increasing carbon number for each pyrolysis duration (Fig. 2(a)), and the relative abundance of short-chain to long-chain *n*-alkene/alkanes increased with pyrolysis duration (Fig. 2(b)). The yield of *n*-alkene/alkane doublets first increased then decreased with increasing pyrolysis duration. Secondary cracking of the *n*-alkyl moieties was evident after 90 s, as is commonly observed in the pyrolysis of geomacromolecules in closed systems.[12,22]

#### *Aromatic hydrocarbons*

The abundance of aromatic hydrocarbons relative to *n*-alkene/ alkanes in the pyrolysates increased rapidly when the pyrolysis duration exceeded 90 s (Figs. 3(a) and 3(b)), suggesting that prolonged pyrolysis duration intensified the cyclization, dehydrogenation and aromatization reactions of the yielded products. It is evident that the ratios of naphthalene/methyl naphthalene and phenanthrene/methyl phenanthrene increased with increasing pyrolysis duration (Fig. 3(c)), which may imply an increasing degree of demethylation for the methyl-substituted aromatic hydrocarbons. These results agree well with those obtained from kerogen pyrolysis at high temperatures in a closed system.[22,23] Demethylation was also evident in the polymethyl-substituted benzenes, as indicated by the increasing ratio of trimethylbenzene to tetramethyl benzene (TMB/TTMB) with increasing pyrolysis duration (Fig. 3(d)). The indane/indene ratio increased slightly as the reaction duration increased from 60 s to 90 s (Fig. 3(c)). However, beyond 90 s a rapid decrease in the ratio was observed, which may have indicated a significant dehydrogenation of the indane.

#### *Tetramethylbenzenes*

The abundance of 1,2,3,4-TTMB in the pyrolysates of oil asphaltenes is significant for the characterization of the oil source.[13] Its relative abundance decreased progressively with increasing pyrolysis duration compared with 1,2,3,5-TTMB (Fig. 3(d)). It has been shown that a suite of kerogens displays a rapid decrease in 1,2,3,4-TTMB with increasing maturity, which suggests the relatively low stability of the precursor of this compound in the kerogen.[24] A recent study has demonstrated a decrease in the concentration of 1,2,3,4-TTMB with increasing thermal level of oil, indicating that it is less stable than 1,2,3,5-TTMB.[25] Therefore, the relative abundance of 1,2,3,4-TTMB in geological samples is affected by both the source and the thermal maturity.

### Variations in carbon isotope ratios of compounds obtained at different pyrolysis durations

A clean *n*-alkane fraction was obtained from the pyrolysates using the purification procedure in this work, which helped ensure that high-precision isotope measurements were obtained (Fig. 4). The $\delta^{13}C$ values of individual *n*-alkanes showed little variation, which is consistent with the results for *n*-alkanes obtained from the same sample by normal pyrolysis methods.[13] In addition, significant $^{13}C$ enrichment was seen in the *n*-alkanes generated at 105 s and 120 s corresponding to their decreasing yield, suggesting that secondary cracking had taken place (Fig. 2). A similar relatively large $^{13}C$ enrichment was also observed for the alkanes yielded from kerogens by pyrolysis in a closed system, where secondary cracking of *n*-alkanes was significant and the relative amount of aromatic hydrocarbons was much greater than that of *n*-alkanes.[23] The $\delta^{13}C$ values of *n*-alkanes generated between 60 s and 90 s normally vary between −35.2 and −34.5 ‰, which is consistent with those released by pyrolysis at 320°C for 3 days.[13] The *n*-alkanes produced at 105 s and 120 s showed higher $\delta^{13}C$ values in the range − 34.0 to −33.5 ‰.

The $\delta^{13}C$ values of 1,2,3,4-TTMB obtained in the present study decreased from −21.3 to −25.4 ‰ with increasing pyrolysis duration (Fig. 5(b)). This compound, released at 60 s and 75 s, had similar $\delta^{13}C$ values (about −21.5 ‰), which were close to those obtained in a previous study (ca −20 ‰) by normal low-temperature pyrolysis.[13] The apparent decrease in the 1,2,3,4-TTMB carbon isotope ratios with increasing
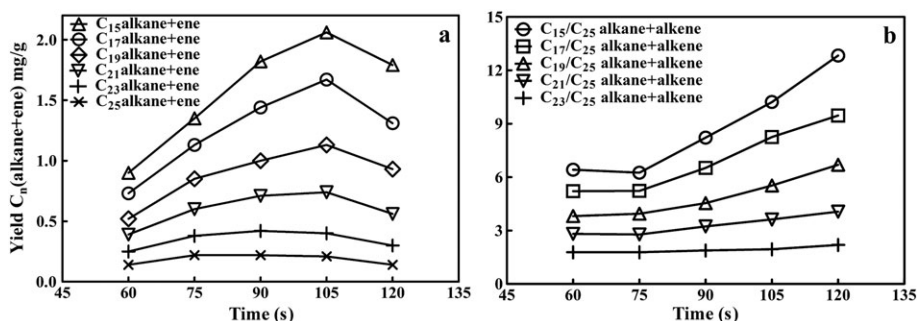


**Figure 2.** (a) Yields of *n*-alkene/alkane doublets with the pyrolysis duration and (b) yield ratios of short-chain *n*-alkene/alkanes to $C_{25}$ *n*-alkene/alkane with pyrolysis duration.
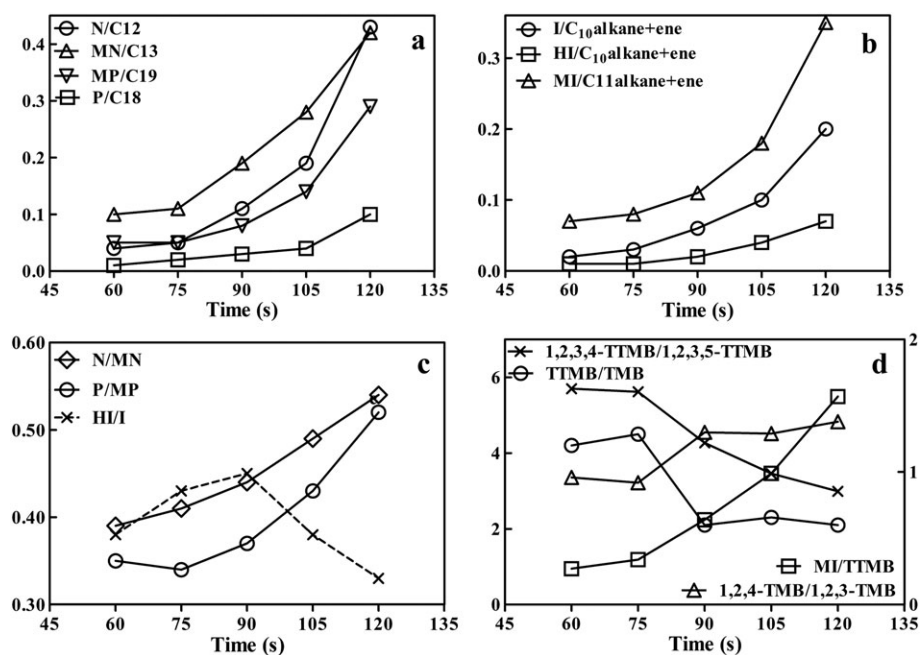
**Figure 3.** Molecular ratios showing changes in the compositions of pyrolysates of asphaltene HD11C obtained at different durations. The peak areas of the *n*-alkene/ alkanes were measured from the TIC chromatograms, while those of the aromatic compounds are from the mass chromatograms of the corresponding characteristic ions. TTMB includes 1,2,3,4- and 1,2,3,5-TTMB; TMB includes 1,2,4-TMB and 1,2,3-TMB. In (d), the MI/TTMB ratios and 1,2,4-TMB/1,2,3-TMB ratios are shown by the right-hand scale of the Y-axis.

pyrolysis duration did not agree with kinetic isotope fractionation from pyrolysis. In carrying out the isotope measurements, the $\delta^{13}C$ values for this compound are easily affected by the adjacent shoulder peak of methyl indene which was observed to partly co-elute with 1,2,3,4-TTMB, and the relatively poor separation between the two compounds may lead to a negative shift in the $\delta^{13}C$ values. In addition, the relative abundance of methyl indene significantly increased when the pyrolysis duration exceeded 75 s (Fig. 3(d)),

corresponding to the rapid decrease in measured $\delta^{13}C$ values for TTMB.

The carbon isotope ratios of the *n*-alkanes and 1,2,3,4-TTMB released by asphaltene HD11C pyrolysis at 60 s and 75 s showed a marked difference (up to 14 ‰), which is indicative of different origins for these two types of molecules.[14] Thus, rapid pyrolysis and subsequent isotope analyses effectively distinguished between the sources of the organic moieties bound in the asphaltenes.
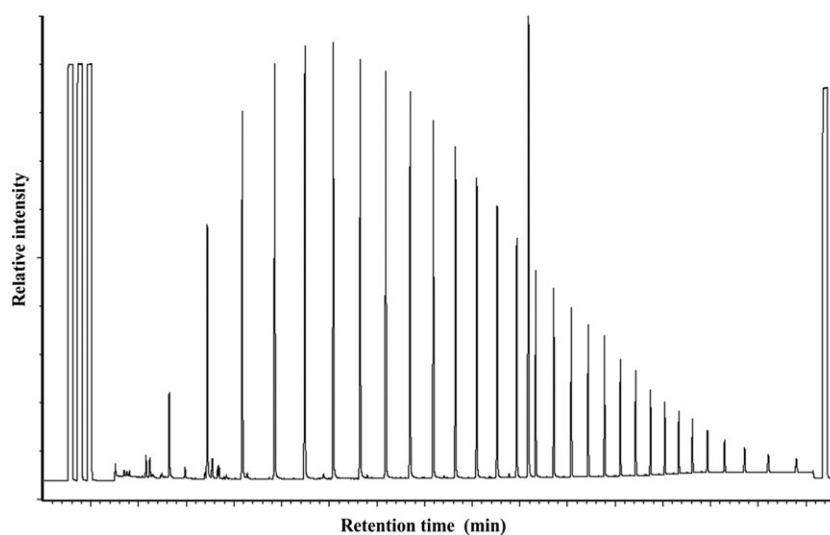


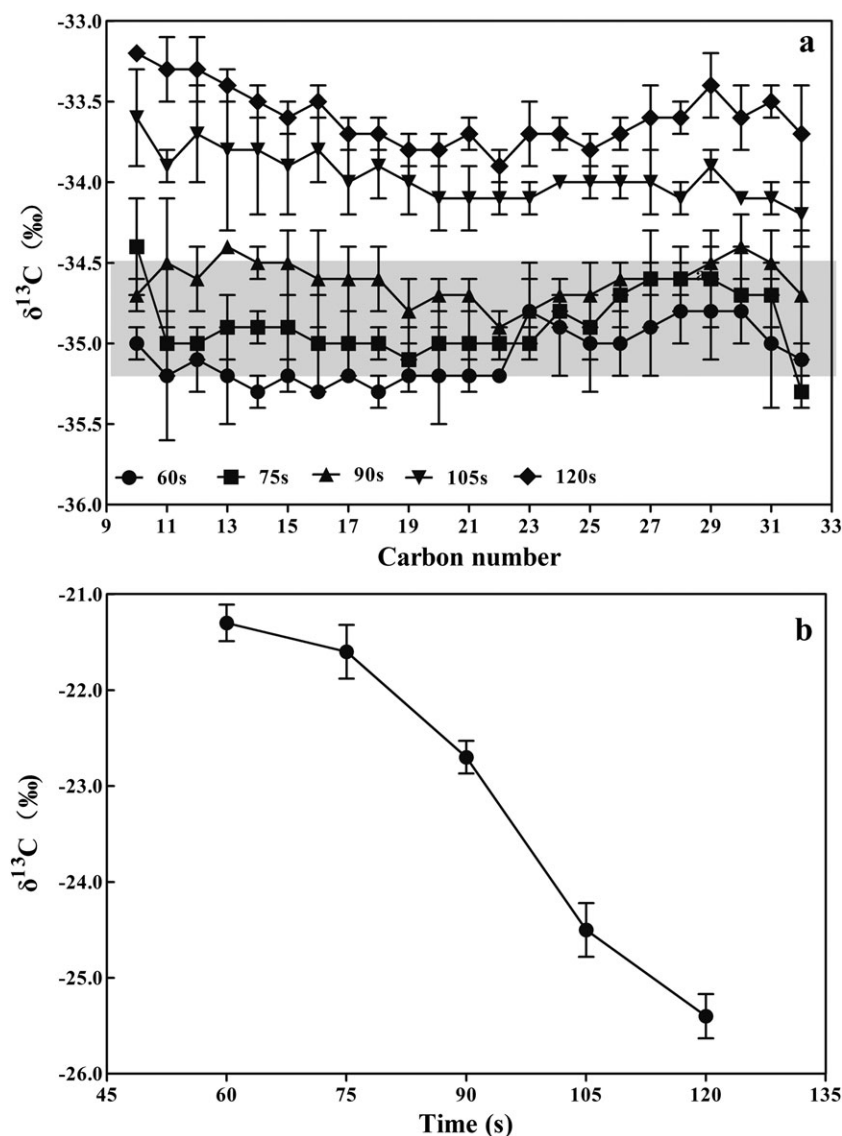**Figure 4.** Purified *n*-alkane fraction displayed by the *m/z* 44 ion chromatograms in carbon isotope measurements.

**Figure 5.** (a) Carbon isotope ratios of *n*-alkanes. Shaded area is the $\delta^{13}$C value range of *n*-alkanes released from normal low-temperature pyrolysis of the same sample.[13] (b) Carbon isotope ratios of 1,2,3,4-TTMB released at different durations. Error bars indicate SD, 1σ, n = 6.

### Carbon isotope analyses of *n*-alkanes released from asphaltenes from various sources

The Tarim Basin in west China and the Bohai Bay Basin in east China are two important petroliferous basins with multiple source layers, and they have attracted continuous geochemical studies of the oil source characteristics and the extent of oil mixing.[17,18] Carbon and hydrogen isotope data for the *n*-alkanes in the oil divide the marine oils from the Tarim Basin into two distinct groups (Fig. 6).[17] Carbon isotope ratios of the *n*-alkanes released from normal low-temperature pyrolysis of asphaltenes separated from group I oils have been reported.[13] In the present study, the asphaltenes were separated from typical group II oils (TD2 and TZ62S, Table 1) and characterized by the proposed rapid pyrolysis method, along with asphaltenes previously analyzed. A recent review suggested that group I oils probably originated from the Cambrian-Lower Ordovician

source rocks, while the origin of group II oils still needs to be clarified.[26] The *n*-alkanes released from five group I asphaltene samples mostly showed $\delta^{13}$C values varying from −36 to −34 ‰, which fall in the range of previously reported group I oil asphaltenes.[14] The *n*-alkanes obtained from group II oil asphaltenes (TD2 and TZ62S) are much more enriched in $^{13}$C (by 4–8 ‰) than those from group I asphaltenes, demonstrating the usefulness of carbon isotope analyses of *n*-alkanes obtained from the proposed pyrolysis procedure.

The *n*-alkanes of different carbon numbers obtained from asphaltene TZ62S showed a small variation in carbon isotope ratios (mostly within 0.5 ‰), which is similar to that of the *n*-alkanes in a saturated fraction of the corresponding oil sample.[17] Although the *n*-alkanes from the saturated fraction of the group II oil, TD2, had almost identical isotope ratios to those in sample TZ62S,[17] by comparison, the *n*-alkanes released from the asphaltene sample TD2 were enriched with
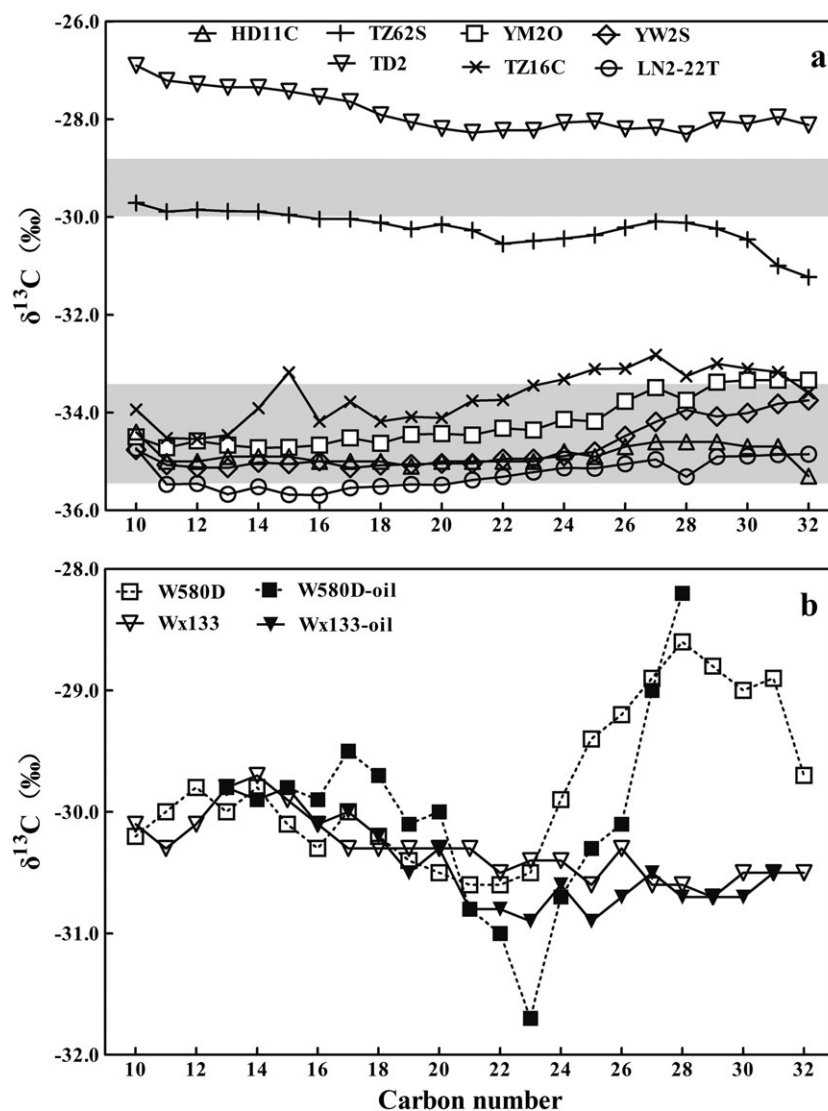
**Figure 6.** Carbon isotope compositions of *n*-alkanes released by pyrolysis of asphaltenes from (a) the Tarim Basin, and (b) the Bohai Bay Basin. All pyrolysis was performed for 75 s. In (a), shaded area shows the $\delta^{13}C$ value ranges of *n*-alkanes in the saturated fraction of oil typical of two groups.[17] In (b), open and filled symbols indicate *n*-alkanes from the asphaltene pyrolysates and saturated fraction of oil, respectively.

$^{13}$C by 2–3 ‰. The total carbon isotope ratio in the asphaltene sample TD2 was higher than that in sample TZ62S by about 1.5 ‰ (Table 1). A relatively intensified thermal effect on oil TD2, resulting from very deep burial in its geological history,[26] could be responsible for the $^{13}$C enrichment of both bulk asphaltenes and their bound organic moieties.

Two lacustrine oil samples from the Bohai Bay Basin showed highly different *n*-alkane carbon isotope profiles, in both the saturated fraction and the asphaltene pyrolysates. The carbon isotope profiles from both the saturated fraction of oil Wx133 and the pyrolysates of the corresponding asphaltene showed a relatively flat pattern with less $^{13}$C enrichment in the short-chain *n*-alkanes than in the long-chain homologues. In addition, the $\delta^{13}C$ values of the *n*-alkanes from these two fractions mainly range between –31 and –30 ‰. Along with the carbon isotope profile, these signatures

correlate with oils from the Eocene Kongdian mudstone source rocks.[18] A further oil sample, W580D, exhibited more complicated results: the *n*-alkanes from the saturated fraction were characterized by a 'V'-shaped carbon isotope profile, and those from the asphaltene pyrolysates showed a similar profile but with less variation in $\delta^{13}C$ values for the *n*-alkanes from $C_{16}$ to $C_{23}$. The $\delta^{13}C$ values of *n*-alkanes with different chain lengths varied from –31 to –28.5 ‰ for the asphaltene pyrolysates, and from –32 to –28 ‰ for the saturated fraction. These characteristics suggest complex sources for the *n*-alkanes in lacustrine oil, which is correlated to the shale in member IV of the Shahejie Formation.[18] Thus, it is evident that the *n*-alkanes from oil asphaltene pyrolysates may show marked differences in both their isotopic signatures and their profiles, which might be related to the isotopic differences of the oil sources.

## CONCLUSIONS

A series of pyrolysis experiments was performed on an oil asphaltene sample in sealed ampoules at 610°C for durations not longer than 120 s. The pyrolysates obtained under these conditions showed products similar to those released by flash pyrolysis. Typical secondary reactions occurring in the closed system became significant for pyrolysis durations longer than 90 s, as indicated by the yields and carbon isotopic signatures of the n-alkanes and the relative abundances of aromatic compounds in the pyrolysates. Hence, a short pyrolysis duration of 75 s was adopted for routine analyses. Two characteristic components in the pyrolysates, namely n-alkanes and 1,2,3,4-tetramethylbenzene, showed highly distinctive $\delta^{13}C$ values consistent with those from normal low-temperature pyrolysis described in previous studies. Furthermore, carbon isotope analysis of the n-alkanes derived from the pyrolysis was demonstrated to be able to effectively distinguish asphaltenes from different sources, inferred from both the isotope profile and the isotopic signatures. The proposed easy-to-use pyrolysis procedure provides an alternative for rapidly obtaining n-alkanes from asphaltenes for carbon isotope analyses, to assist in 'oil–source' and 'oil–oil' correlation studies.

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