

## D/H ratio analysis of pyrolysis-released *n*-alkanes from asphaltenes for correlating oils from different sources



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### ABSTRACT

When oil has been greatly altered by severe biodegradation, asphaltene pyrolysis is commonly conducted to obtain intact *n*-alkanes for carbon isotope analysis, through which oil source characterization and oil–oil correlations can be performed. The ratio of hydrogen isotopes deuterium and hydrogen (D/H ratio) in the individual *n*-alkanes of oil maltenes has been shown to indicate differences between the depositional environments of the oil sources. The utility of the D/H ratio analysis of *n*-alkanes from the asphaltene pyrolysis for oil correlation need to be demonstrated. In this study, 18 asphaltene samples from different sources were collected and isothermally pyrolyzed in sealed gold tubes. Effects of the pyrolysis temperature were first illustrated for molecular ratios of alkanes and aromatic compounds and for D/H ratios of pyrolysis-yielded *n*-alkanes. In the case of *n*-alkanes in oil maltenes being unavailable for analysis after severe biodegradation, the D/H ratio range of the *n*-alkanes from the asphaltene pyrolysis was found to be consistent both in normal and biodegraded oils from the same source, indicating that biodegradation has had little effect on their hydrogen isotope signatures. In addition, *n*-alkanes yielded by asphaltenes from different sources possess clearly different D/H ratios, enabling *n*-alkane correlation between maltenes that are otherwise very similar. However, relatively large differences of D/H ratios can exist between *n*-alkanes in the asphaltene pyrolyzates and in maltenes, once the oil was altered by oil mixing formed at different maturity levels. The proposed method is thus helpful in oil–oil correlation for significantly biodegraded oil and oil from a mixed origin.

### 1. Introduction

Oil was produced from thermal degradation of kerogen in source rocks, then left kerogen and migrated into reservoirs. Being a complicated mixture, oil can be divided into soluble maltenes and insoluble asphaltenes based on the solubility in low molecular alkanes. Asphaltenes are the largest organic moieties in oil. Pyrolysis studies have revealed a similarity between molecular units in asphaltenes and source kerogens [1]. The high molecular weight of asphaltenes makes it more highly resistant to biodegradation than the hydrocarbons in maltenes [2]. When evidence indicates significant influence of secondary processes on the compounds in oil maltenes (e.g., biodegradation, evaporation: [3–5]), carbon isotope analysis of the individual compounds released by the asphaltene pyrolysis shows that the alteration of asphaltenes by secondary processes is minimal [6–9]. The ratios of hydrogen isotopes deuterium and hydrogen (D/H ratios) of individual compounds in maltenes have been found to provide information about the paleoclimate and depositional environment of the

oil source [10,11]. Hydrogen isotope analysis of individual compounds in maltenes has been applied in various fields of oil geochemistry, such as characterization of the oil source [10–12] and for carrying out oil–source and oil–oil correlations [13–15]. In organic molecules in the oil system, the D/H ratios are primarily related to the source characteristics and have been altered by a combination of isotope exchange, maturation, and secondary processes [16,17]. Nonetheless, hydrogen isotope analysis of asphaltene pyrolyzates has not previously been performed.

The present study is aimed at investigating the relationships between the D/H ratios of *n*-alkanes in maltenes and in asphaltene pyrolyzates from the same oil, and between asphaltenes from non-biodegraded oil and from severely biodegraded oil. Asphaltenes were isolated from 18 oil samples from sources in distinct depositional environments, some of which have been greatly altered by biodegradation. The D/H ratios of the *n*-alkanes released by the pyrolysis of oil asphaltenes were measured and compared with the D/H ratios in *n*-alkanes from the oil maltenes. Variations in the D/H ratios of the *n*-alkanes in asphaltene

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**Table 1**  
Asphaltenes in marine oils from the Tarim Basin (#1–13) and in terrestrial oils from the Bohai Bay Basin (#14–18).

No.	Sample	Strata	Depth (m)	Type	Biodegradation <sup>a</sup>	Group <sup>b</sup>	$\delta D_{n\text{-mal}}$ <sup>c</sup>	$\delta D_{n\text{-asp}}$ <sup>d</sup>
1	LN2T	Triassic	–	Normal oil	Light	I	–95	–111
2	LN58T	Triassic	–	Normal oil	Light	I	–96	–117
3	HD11C	Carboniferous	5125–5128.5	Heavy oil	Light	I	–101	–114
4	TZ10C	Carboniferous	4206–4226	Normal oil	Light	I	–100	–117
5	TZ401C	Carboniferous	3244–3247	Normal oil	Light	I	–98	–101
6	TZ2C	Carboniferous	3870–3883	Heavy oil	Light	I	–98	–108
7	YM2O	Ordovician	5940–5953	Normal oil	Light	I	–103	–120
8	YW2O	Ordovician	5460–5463	Normal oil	Light	I	–105	–119
9	TZ31S	Silurian	4594.4	Tar sands	Heavy–severe	I	–	–122
10	HA1S	Silurian	6080.0	Tar sands	Severe	I	–	–124
11	HD11S	Silurian	5353.1	Tar sands	Severe	I	–	–120
12	YW2S	Silurian	5211.2	Tar sands	Severe	I	–	–123
13	TD2	Cambrian	4561–5040	Heavy oil	Light	II	–142	–164
14	W580D	Tertiary	3167.8–3177.8	Normal oil	None	–	–132	–138
15	WX133	Tertiary	3179.4–3185.8	Normal oil	None	–	–147	–155
16	W46	Tertiary	2996.6–3036.8	Normal oil	None	–	–141	–143
17	G894	Tertiary	3344.5–3378	Normal oil	None	–	–157	–170
18	ZX792	Tertiary	3496.9–3505.4	Normal oil	None	–	–168	–166

<sup>a</sup> Biodegradation level was determined according to the relative content of 25-norhopanes and *n*-alkanes in maltenes of oil or tar sand extracts reported by [9,15].

<sup>b</sup> Grouping of oil from the Tarim Basin was based on hydrogen isotope ratios of *n*-alkanes in maltenes [15]. For Silurian tar sands, oil grouping was based on the carbon isotope ratios of *n*-alkanes released from the pyrolysis of asphaltenes [9] since most of *n*-alkanes in maltenes had been degraded.

<sup>c</sup>  $\delta D_{n\text{-mal}}$  denotes weighted mean  $\delta D$  values of *n*-alkanes in maltenes of oil, and data for samples #1 and #14–18 were obtained in this study. Data for samples #2–8 and #13 were reported by [15], and data for samples #9–12 were not analyzed due to general absence or very low content of *n*-alkanes in maltenes after heavy or severe biodegradation.

<sup>d</sup>  $\delta D_{n\text{-asp}}$  denotes weighted mean  $\delta D$  values of *n*-alkanes in asphaltene pyrolyzates, and data for all samples were obtained in this study.

pyrolyzates with the oil sources were also investigated.

## 2. Material and methods

### 2.1. Samples

Oil samples were mainly collected from the Tarim Basin in north-western China, and a few samples were also collected from the Bohai Bay Basin in eastern China for comparison (Table 1). Extensive geochemical studies of oil in these basins have previously been reported, because the presence of multiple source layers and secondary processes have made correlating oil and elucidating oil mixing very difficult [18–21].

The Tarim Basin is well known in China for its deep to ultra-deep oil accumulation (3000–6000 m, sample 1–13, Table 1), originating mainly from Cambrian–Ordovician marine source rocks [18]. Two types of oil were collected from the Tarim Basin, one of heavy and normal oils [15,19] and one of severely biodegraded bitumen in Silurian tar sands, suggested by the abundant 25-norhopanes and very low content of *n*-alkanes [9].

The Bohai Bay Basin is one of the key regions in China that produces oil (sample 14–18) sourced from Tertiary lacustrine shales or mudstones [20,21]. Three major source layers are present in the fourth and third members (abbreviated as Es<sub>4</sub> Member and Es<sub>3</sub> Member) of the Eocene–Oligocene Shahejie Formation and the Paleocene–Eocene Kongdian Formation (abbreviated as E<sub>k</sub> Formation). As such, oil grouping and recognizing mixing of oil from different sources has been an important task for geochemists. The three source layers have been shown to display distinctive  $\delta^{13}\text{C}$  profiles for *n*-alkanes with different numbers of carbon atoms, with the large differences depending on both the source organism and the depositional environment [20,21].

### 2.2. Experimental analysis

About 1 g of oil or extracted bitumen was dissolved in 2 mL dichloromethane, and asphaltene was precipitated by adding a 40-fold volume of *n*-hexane to the dichloromethane solution. After filtration, crude asphaltenes were purified by Soxhlet extraction with *n*-hexane for 3 days. For compound-specific isotope analysis of *n*-alkanes from asphaltenes, isothermal pyrolysis in a closed system [6–9] is commonly

preferred to programmed-temperature pyrolysis [22]. Asphaltene pyrolysis was carried out by placing approximately 50 mg of asphaltene powder into a gold tube (50 mm × 6 mm i.d.), which was sealed in an argon atmosphere and subjected to isothermal pyrolysis for 72 h. Asphaltene sample #LN2T from the Tarim Basin was pyrolyzed at 280, 300, 320, 350 and 380 °C to investigate the effect of temperature on the D/H ratios in the released *n*-alkanes. For convenience of comparison, all the asphaltene samples were pyrolyzed at 320 °C for isotope analysis.

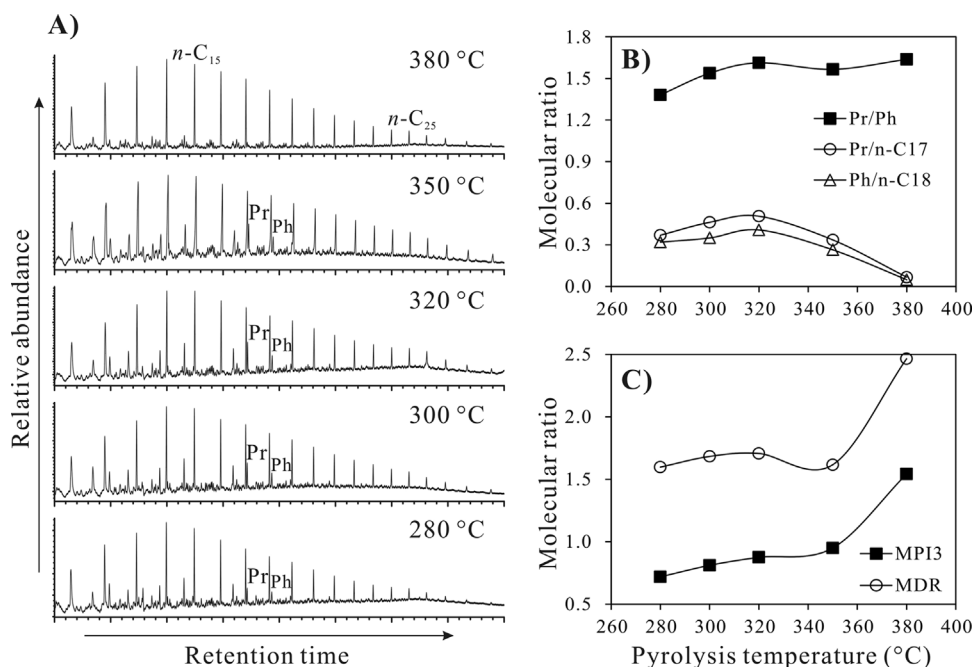
After cooling, the outer surface of the gold tube was ultrasonically cleaned with dichloromethane. Cleaned tubes were refrigerated at –18 °C for 1 h, then opened as soon as possible and loaded into a 4 mL sample vial containing about 1.5 mL of *n*-hexane. The vial was then sealed with a cap equipped with a polytetrafluoroethylene/silicone septum. Pyrolyzates in the gold tube were ultrasonically extracted for 20 min using *n*-hexane, then filtered and fractionated on silica gel in a micro-column (10 cm × 6 mm i.d.). The saturated and aromatic hydrocarbons were eluted with *n*-hexane and *n*-hexane/dichloromethane (3:2, v/v), respectively. After gas chromatography-mass spectrometry (GC–MS) analysis, saturated hydrocarbons were further purified to obtain linear alkanes by 5 Å molecular sieving for isotope analysis [23].

GC–MS analyses of the oil asphaltene pyrolyzates were performed by a Thermo DSQII mass spectrometer to which a Trace Ultra gas chromatograph was interfaced. Compound-specific carbon and hydrogen isotope analysis was performed on a GV isoprime isotope ratio mass spectrometer (IRMS) and on a Finnigan™ Delta<sup>plus</sup> XL IRMS connected to a HP 6890 gas chromatograph via a combustion interface and a high-temperature conversion interface. Detailed conditions used for GC–MS and GC-IRMS analysis were similar to those in [15]. A mixture of *n*-alkanes (obtained from Dr. A. Schimmelmann, Indiana University) was routinely measured to monitor the overall system. Each sample was analyzed in duplicate or triplicate. Analytical precision was generally better than 0.5‰ (± 1σ) for carbon isotope analysis and 5‰ (± 1σ) for hydrogen isotope analysis.

## 3. Results and discussion

### 3.1. Variation in $\delta D$ values of *n*-alkanes with pyrolysis temperature

A recent review [24] has indicated that asphaltene aggregates usually occlude some hydrocarbons which would be released upon



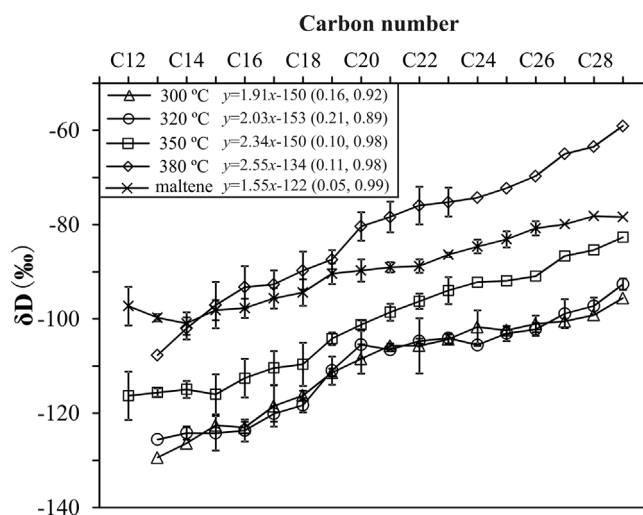
**Fig. 1.** A) Total ion current (TIC) chromatograms of saturated hydrocarbons separated from pyrolyzates of asphaltenes #LN2T at different temperatures for 3 days in sealed gold tubes. B) and C) show the molecular ratios of the saturated and aromatic compounds.

$n$ -C<sub>15</sub> and  $n$ -C<sub>25</sub> denote carbon numbers of the  $n$ -alkanes. Pr = pristane, Ph = phytane. MPI3 = (3 + 2-)/(9 + 1-) methylphenanthrene (MP), MDR = 4-/1-methyldibenzothiophene (MDBT).

pyrolysis besides asphaltene-bound molecules. Multiple charge events related to the source layers and thermal histories resulted in distinct carbon isotope ratios between  $n$ -alkanes occluded by asphaltenes and in maltenes from the Tarim Basin [25]. Fractions occluded by asphaltenes contained abundant  $n$ -alk-1-enes series beside  $n$ -alkanes [25]. However, the  $n$ -alk-1-enes series were hardly detected from the asphaltene pyrolyzates obtained at different temperatures (Fig. 1). Therefore, products from asphaltene pyrolysis in a closed system over 3 days are generally assumed to be mainly from the bound structures of asphaltenes.

Distributions of  $n$ -alkanes in saturated hydrocarbons isolated from the pyrolyzates of asphaltenes #LN2T show little changes as pyrolysis temperature increases and are unimodal with a peak at C<sub>14</sub> (Fig. 1A). The expected increase in the relative content of short-chain  $n$ -alkanes was not observed with elevated pyrolysis temperature, which may be due to evaporation loss during the recovery of pyrolyzates and subsequent fraction separation. The ratios of isoprenoid alkanes (pristane and phytane) to  $n$ -alkanes first increase slightly, then show a remarkable drop at a pyrolysis temperature of 350 °C, and finally are nearly zero at 380 °C (Fig. 1B). Oil pyrolysis experiments performed in a similar manner to this study have revealed that the disappearance of isoprenoid alkanes took place at an equivalent reflectance (Ro) of 1.3%, and the contents of the long-chain  $n$ -alkanes (> C<sub>16</sub>) began to decrease simultaneously [26]. A recent experimental study also shows  $n$ -alkanes released by kerogen pyrolysis in a closed system began to secondarily crack with an equivalent Ro increasing from 1.1% to 1.4%, which is consistent with the rapid increase of molecular maturity indices based on polycyclic aromatic compounds [27]. Two maturity indices, calculated using relative content of methylphenanthrene and methyldibenzothiophene isomers, were observed to rapidly increase from 350 °C to 380 °C (Fig. 1C). Therefore, we infer that the secondary cracking of pyrolyzates became notable during this interval.

The yield of  $n$ -alkanes from pyrolysis at 280 °C is too low for hydrogen isotope analysis, so only isotope data obtained at temperatures of 300–380 °C were shown (Fig. 2). Three basic characteristics of hydrogen isotopes were noted for pyrolysis-released  $n$ -alkanes from asphaltenes at different temperatures. First, the D/H ratios of the  $n$ -alkanes released by asphaltene pyrolysis and from oil maltenes both displayed right-upward curves (Fig. 2), as is commonly seen in  $n$ -alkanes in oil and in sediments coming into the oil window [10,11,15,28]. Second, the  $n$ -alkanes produced by asphaltene pyrolysis



**Fig. 2.**  $\delta$ D values of  $n$ -alkanes in maltenes and in asphaltene pyrolyzates at different temperatures for 3 days in sealed gold tubes (sample #LN2T), together with linear regression equations for the average  $\delta$ D from triplicate analyses with respect to carbon number (C<sub>15</sub>–C<sub>28</sub>). Two numbers in the brackets after each equation denote the standard error on the slope and the square of correlation coefficient.

at 300 °C and 320 °C have consistent hydrogen isotopic compositions, and become progressively enriched in D at temperatures above 320 °C (Fig. 2). Significant D enrichment was found in  $n$ -alkanes released at 380 °C. A large increase in the D content of  $n$ -alkanes at relatively high temperatures has been noted with regard to the pyrolysis of oil or kerogen in anhydrous closed systems [26,27]. Third, the slope of the  $\delta$ D profile generally increases at higher pyrolysis temperatures (Fig. 2), which is similar to a previous observation on oil pyrolysis in sealed gold tubes [26]. Tang et al. [26] suggested that the kinetic isotopic effects during oil cracking are the main cause of these characteristics. Alkane molecules containing light isotope H were released first from asphaltene bound structures due to the kinetic isotope effect, which would result in a generally higher enrichment of D in  $n$ -alkanes with increasing pyrolysis temperature. On the other hand, the short-chain  $n$ -alkanes were also derived from secondary cracking of the long-chain  $n$ -alkanes produced by asphaltenes. This process thus leads to further enrichment of D in the residual long-chain  $n$ -alkanes and produced

short-chain *n*-alkanes, which are relatively depleted in D, at the same time. Therefore, the long-chain *n*-alkanes in the closed pyrolysis system were more and more enriched in D relative to their short-chain homologues with intensified cracking, leading to an increase in the slope of the  $\delta D$  profile of *n*-alkanes. However, isotope exchange with inorganic hydrogen (e.g., in water) is a major factor affecting the hydrogen isotope compositions of *n*-alkanes in oil or sediments under geological conditions [16,17]. This buffer effect means the increasing slope of the  $\delta D$  profile of *n*-alkanes in oil with increasing thermal maturity may be not as evident as that observed in the anhydrous pyrolysis experiments. Fig. 1 shows that even at the relatively low temperatures of 300 °C and 320 °C, the slopes are clearly greater than for *n*-alkanes in the oil maltenes.

### 3.2. $\delta D$ values of *n*-alkanes in marine oil asphaltenes from the Tarim Basin

The Tarim Basin is one of the largest producing regions in China for oil originating in marine strata. Multiple source layers in the old Cambrian–Ordovician strata and a complicated tectonic history have resulted in significant effects of many secondary processes on both the chemical and physical properties of the oil in the basin, such as thermal cracking, biodegradation, and oil mixing [18]. Oil from this basin was classified into two major groups based on D/H ratios of *n*-alkanes in oil maltenes [15]: one is characterized by relatively heavy  $\delta D$  values (sample 1–8, group I) and another one shows relatively light  $\delta D$  values (sample 13, #TD2, group II), suggesting distinct sources for the two groups. Most *n*-alkanes in the extract maltenes from the Silurian tar sands have been lost due to heavy to severe biodegradation, so their D/H ratios of *n*-alkanes were not measured (sample 9–12, Table 1). Pyrolysis-released *n*-alkanes from asphaltenes in the group I oils and the extracts from the Silurian tar sands have consistent  $\delta^{13}C$  ranges from –36‰ to –33‰ [9,19], so the extracts were also classified into group I (Table 1).

Consistent with these observations, pyrolysis-released *n*-alkanes from the asphaltenes of group I have  $\delta D$  values ranging from –140‰ to –90‰, while those from asphaltenes #TD2 have much lighter  $\delta D$  values from –170‰ to –160‰ (Fig. 3). Moreover, *n*-alkanes in the pyrolyzates from sample #TD2 show much less variation in D/H ratios with increasing carbon number relative to those samples of group I. The

oil #TD2 was formed ~450 Ma ago and endured later thermal alteration in the reservoir at temperatures higher than 200 °C [18,29]. Oil cracking led to significant D enrichment in *n*-alkanes, as shown in an experimental study [26]. However, the D/H ratios of *n*-alkanes in sample #TD2 are much lighter than those in samples from group I, suggesting that the strong thermal alteration did not completely eliminate the differences in the hydrogen isotopic signatures relating to the oil sources. The original biological signals are not expected to be preserved through petroleum hydrocarbons due to extensive hydrogen exchange [12,16,17,28]. Nevertheless, D/H ratios of *n*-alkanes yielded by asphaltene pyrolysis are primarily related to the source characteristics. Thus, D/H ratios of pyrolysis-released *n*-alkanes from asphaltenes can be used for oil correlation as well as the carbon isotope ratios.

Biodegradation is commonly observed on group I marine oils from the Tarim Basin due to multiple tectonic events [9,15,18,30,31]. However, the biodegradation level varies greatly with individual oil samples. Selected oil and bitumen samples from which asphaltenes were isolated in this study ranged from light biodegradation to severe biodegradation (sample 1–13, group I, Table 1), as determined by reported relative contents of 25-norhopanes and *n*-alkanes [9,15]. The *n*-alkanes in oil maltenes are increasingly enriched in D up to 40‰ as biodegradation increases [4,5]. As shown in Fig. 3, the hydrogen isotopic signatures of *n*-alkanes released from these asphaltenes are generally similar for both the bitumen severely altered by biodegradation and oil. Therefore, for the biodegradation range investigated in this study, the D/H ratios of pyrolysis-yielded *n*-alkanes from asphaltenes are little affected by severe biodegradation. As stated above, most *n*-alkanes in maltenes from the Silurian tar sand were lost and useless for the D/H ratio analysis. In such cases, hydrogen isotope analysis of pyrolysis-released *n*-alkanes from asphaltenes is more advantageous for oil–oil correlation than that of maltenes.

The average  $\delta D$  values of *n*-alkanes from the asphaltene pyrolyzates were ~20‰ less than from *n*-alkanes in maltenes for the group I oils, which is evidenced by the short-chain *n*-alkanes (Fig. 3). Oil mixing is a common phenomenon for group I oils from the Tarim Basin [15,18,31]. As a result, *n*-alkanes in maltenes and asphaltenes were probably derived from different oil charges, either from different sources or from different maturity stages of the same source. Even if they were originated from the same source, asphaltenes were isolated mainly from relatively low-maturity heavy and normal oils, while *n*-alkanes in maltenes could be mixed with those produced later [15,18]. Previous research has shown that *n*-alkanes in maltenes of the later-charged oil were more enriched in D due to being produced at relatively high maturity [15], such that D enrichment in *n*-alkanes from asphaltenes is less than that in *n*-alkanes in oil maltenes. Therefore, the isotopic signatures of *n*-alkanes yielded by the asphaltene pyrolysis possibly indicates oil asphaltenes were generated earlier than expelled from the source rock compared to the oil maltenes, when considering the influence of oil mixing formed at different maturity levels. D/H ratio analysis of asphaltene-released *n*-alkanes is thus more suitable to establish the isotopic characteristics of oils formed early and to determine a maturity trend of oils from the same source.

### 3.3. $\delta D$ values of *n*-alkanes in lacustrine oil asphaltenes from the Bohai Bay Basin

Oil from the Bohai Bay Basin has been categorized into three major families based on biomarker characteristics and carbon isotope profiles of their *n*-alkanes [20,21]. Distinct carbon isotope profiles of *n*-alkanes in the oil maltenes are believed to be mainly controlled by the carbon isotopic signatures of sources and the depositional environment [20,21]. The carbon isotope ratios of samples #WX133 and #W580D were re-analyzed using the methods described in this study and were found to be consistent with those in a previous study [32]. Both carbon and hydrogen isotope ratios of the other three samples were obtained only in this study.

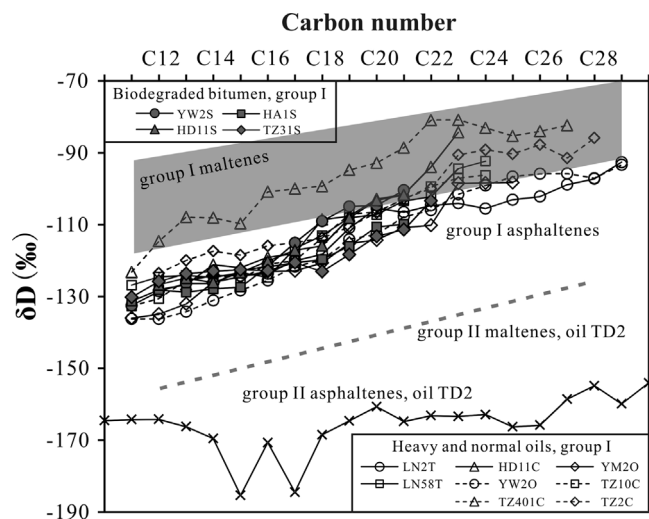


Fig. 3.  $\delta D$  values of *n*-alkanes in asphaltene pyrolyzates from oil and severely biodegraded bitumen from the Tarim Basin.

Pyrolytic condition: 320 °C for 3 days in sealed gold tubes.

Four Silurian tar sand samples that endured heavy to severe biodegradation are denoted by the shaded symbols, while other normal samples were denoted by the blank and cross symbols. For comparison, the shaded belt and grey, dashed line shows the range of  $\delta D$  values of *n*-alkanes in maltenes of group I and group II oils [15] from the Tarim Basin, respectively.

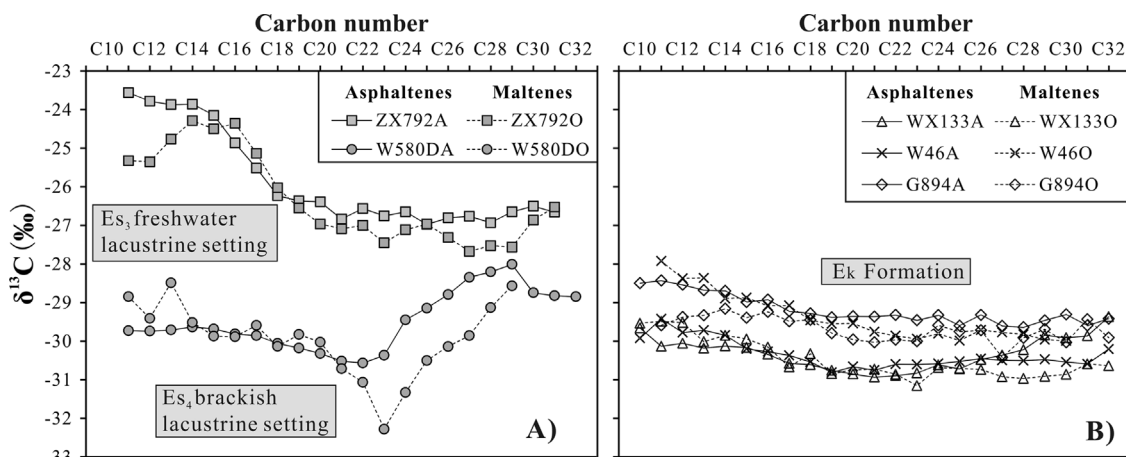


Fig. 4.  $\delta^{13}\text{C}$  values of  $n$ -alkanes in the maltenes (dashed lines) and in the asphaltene pyrolyzates (solid lines) from the Bohai Bay Basin.

Pyrolytic condition: 320 °C for 3 days in sealed gold tubes. Re-analyzed results for samples #WX133 and #W580D using methods in this study are consistent with those in a previous study [32].

The  $n$ -alkanes released from oil asphaltenes can generally be correlated with  $n$ -alkanes in oil maltenes in terms of the distributions of carbon isotope ratios with carbon number. The V-shaped carbon isotope profile of  $n$ -alkanes from oil originating in the Es<sub>4</sub> Member of the Shahejie Formation (sample #W580D, Fig. 4A), which was deposited in a brackish lacustrine environment, has its lowest point at C<sub>23</sub>. Oil originating from the Es<sub>3</sub> Member is characterized by  $^{13}\text{C}$ -enriched  $n$ -alkanes (sample #ZX792, Fig. 4A), with  $\delta^{13}\text{C}$  values ranging from  $-28\text{‰}$  to  $-22\text{‰}$  and a right-downward isotope profile. Source rocks in the Es<sub>3</sub> Member were deposited in a freshwater lacustrine setting. Oil re-entrained in the Ek Formation shows slight  $^{13}\text{C}$  depletion in  $n$ -alkanes with increasing carbon number (#WX133, #W46 and #G894, Fig. 4B).  $\delta^{13}\text{C}$  values for the  $n$ -alkanes generally varied from  $-31\text{‰}$  to  $-28\text{‰}$ , which partially overlaps the Es<sub>4</sub> Member profile.

$\delta\text{D}$  values for  $n$ -alkanes derived by asphaltene pyrolysis are almost identical to those in the maltenes of the related oil (#W580D, #W46), although they differ slightly (within 10‰) from the  $\delta\text{D}$  for  $n$ -alkanes in the maltenes of oil #ZX792 and #WX133 (Fig. 5). The small difference may be attributed to the errors of hydrogen isotope analysis (standard deviation = 5‰). Only sample #G894 showed notable differences (up to 20‰) in the C<sub>18</sub>–C<sub>23</sub> and C<sub>27</sub>–C<sub>32</sub> ranges (Fig. 5B). Compared with the oil from the Tarim Basin, oil samples from the Bohai Bay Basin were not reported to be greatly altered by thermal alteration and biodegradation, and the differences between the D/H ratios of  $n$ -alkanes in asphaltene pyrolyzates and in maltenes are relatively small.

The  $n$ -alkanes from the maltenes and asphaltene pyrolyzates in

sample #W580D (Es<sub>4</sub> brackish lacustrine source) were generally enriched in D by about 30‰ compared to those from oil #ZX792 (Es<sub>3</sub> freshwater source, Fig. 5A). The two oil samples from the Ek Formation (#WX133 and #W46) have  $n$ -alkanes with intermediate  $\delta\text{D}$  values. The D/H ratios in the  $n$ -alkanes from oil #G894 roughly overlap those from oil #ZX972. Overall, the hydrogen isotope compositions of  $n$ -alkanes from the Bohai Bay Basin, both in the maltenes and asphaltenes, fall within the range reported for terrestrial source rocks [11,13,33]. The  $n$ -alkanes extracted from the Es<sub>4</sub> source rock are generally more enriched in D than those from Es<sub>3</sub> shale, which can be attributed to the distinct lacustrine environments whose D/H ratios might have differed greatly, influencing the hydrogen isotope signatures of the organic matter [33]. The different D/H ratios in the  $n$ -alkanes for oils from the Es<sub>4</sub> and Es<sub>3</sub> members of the Shahejie Formation (Fig. 5A) are consistent with those observations. These results thus demonstrate that hydrogen isotope analysis of pyrolysis-released  $n$ -alkanes from asphaltenes can also be adapted for correlating terrestrial oils.

#### 4. Conclusions

Asphaltenes in normal and severely biodegraded oils from old marine source rocks in the Tarim Basin and in normal oils from lacustrine mudstones in the Bohai Bay Basin were subjected to anhydrous pyrolysis in a closed system to investigate the usefulness of the D/H ratios of the released  $n$ -alkanes. The D/H ratios of  $n$ -alkanes from the asphaltene pyrolysis of can be used to classify oils originated from

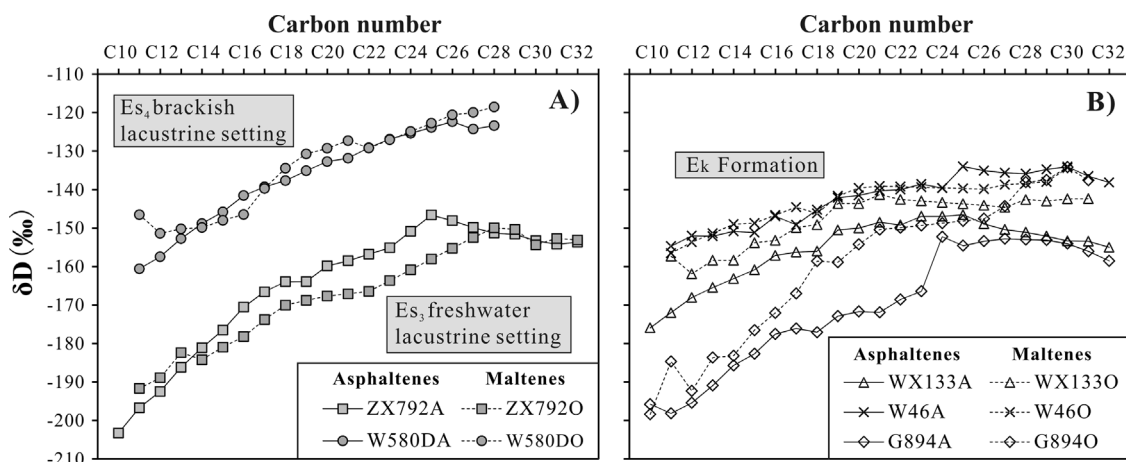


Fig. 5.  $\delta\text{D}$  values of  $n$ -alkanes in the asphaltene pyrolyzates (solid lines) and in the maltenes (dashed lines) from the Bohai Bay Basin.

Pyrolytic condition: 320 °C for 3 days in sealed gold tubes.

marine and terrestrial sources.  $\delta D$  values of pyrolysis-derived *n*-alkanes from normal marine oils have the same range as those from severely biodegraded bitumen that shares a common source with the normal oil. Relatively large differences in the D/H ratios can exist between *n*-alkanes in asphaltene pyrolyzates and in maltenes if the oil mixing formed at different maturity levels, suggesting that hydrogen isotope analysis of asphaltene-released *n*-alkanes is more suitable for determining isotopic characteristics of early-charged oils. Therefore, hydrogen isotope analysis of pyrolysis-derived *n*-alkanes provides an alternative tool for characterizing oils from various origins, especially in cases where the oil has been greatly altered by a secondary process, such as biodegradation and oil mixing.

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