

# Hydrogen isotopic compositions, distributions and source signals of individual *n*-alkanes for some typical crude oils in Lunnan Oilfield, Tarim Basin, NW China

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**Abstract** Isotopic compositions of carbon-bound hydrogen in individual *n*-alkanes from several typical crude oil samples from Lunnan Oilfield, Tarim Basin, NW China, were firstly measured using newly developed gas chromatography-thermal conversion-isotope ratio mass spectrometry. The similar range of  $\delta D$  of individual *n*-alkanes of crude oils among reservoirs of different geological times reflects that hydrocarbons are all derived from the same marine depositional environment. Compared to the theoretic value ( $-150\text{‰}$ ) and the reported  $\delta D$  values ( $nC_{13}$ – $nC_{27}$ ,  $-160\text{‰}$ – $-90\text{‰}$ ) of individual *n*-alkanes for Ordovician-sourced crude oils in the Canadian Williston Basin, the hydrogen isotopic composition of individual *n*-alkanes in crude oils from Lunnan Oilfield is characterized by heavy hydrogen isotopic values ( $nC_{12}$ – $nC_{27}$ ,  $-120\text{‰}$ – $-60\text{‰}$ ). In terms of the factors that control the fractionation of hydrogen isotopes, relatively saline depositional environment and higher thermal maturation were attributed to the heavy  $\delta D$  values of individual *n*-alkanes in crude oils from Lunnan Oilfield.

**Keywords:** hydrogen isotopes, individual *n*-alkanes, distribution, hydrocarbon source, Lunnan Oilfield.

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Petroleum mainly comprises carbon and hydrogen elements. The stable carbon isotopic analysis for whole oil was undertaken as early as the 1930s. After decades, the stable carbon isotopic analytical methods have been developed from analysis for whole oil and oil fractions (e.g., saturated, aromatic and polar fractions) into compound-specific isotopic analysis with the emergence of the newly developed GC-C-IRMS analytical technique. Especially, by using compound-specific isotopic analytical methods at molecular level, the diverse factors that influence carbon isotopic compositions of oils can be dissected<sup>[1]</sup> to allow

us to produce more straightforward interpretations about their origins<sup>[2–4]</sup>, which revealed the technical advantages.

Stable hydrogen isotopic analyses have been widely conducted for studies of coal<sup>[5,6]</sup>, oil<sup>[7–11]</sup> and natural gas<sup>[12,13]</sup>. Particularly, the stable hydrogen isotopic analyses of oils have also been integrated with stable carbon isotopic analyses to enhance the accuracy of source assignments<sup>[10,14]</sup>. Compared to the stable carbon isotopic compositions, hydrogen isotopic compositions have two distinct advantages. One is that the

$\delta D$  values theoretically have the largest variation range due to the largest variations in the relative mass number among all the elements. The other is that the stable carbon isotopic ratios can reflect the characteristics of carbon cycle and diagenetic process, while the stable hydrogen isotopic ratios can reflect the characteristics of water cycle and diagenetic process. For example, Scholl (1984a) has suggested that the  $\delta D$  values of whole oils are effective for differentiating among oils as derived respectively from source rocks of carbonate, shale and marl facies<sup>[10]</sup>, which reveal the potential application advantage of stable hydrogen isotopic analyses. In view of these points, stable hydrogen isotopic analyses of individual *n*-alkanes for crude oils can play an important role in the studies of source assignment and selection of prospection targets.

However, analysis and application of compound-specific hydrogen isotopic compositions are not so wide as that of individual stable carbon isotopic analyses. Few studies on hydrogen isotopic compositions of individual compounds were involved ever since Li et al. (2001) reported the hydrogen isotopic compositions of *n*-alkanes and acyclic isoprenoids alkanes of crude oils from Canadian Alberta and Williston sedimentary basins<sup>[15]</sup>. In this paper we will first measure the hydrogen isotopic compositions of *n*-alkanes for some typical crude oil samples from Lunnan Oilfield, Tarim Basin, and then tentatively discuss their applications in petroleum geochemistry.

## 1 Samples and experiments

Six oil samples were selected for hydrogen isotopic analyses, they include two Triassic-aged oils from Lunnan 23 well (4642–4651 m) and Lunnan 14 well (4609.75–4625 m), and four Ordovician-aged oils from Lunnan 44 well (5283–5323), Lunnan 46 well (6119–6144), Lunnan 10 well (5349–5381 m) and Shacan 2 well (5363–5391 m), and are composed of waxy oils, light oils and heavy oils, which are representative of the diverse range of oil types in Lunnan region. Asphaltenes for all oils were removed by precipitation with *n*-hexane followed by filtration. The deasphalted oils were then separated into saturated, aromatic and polar (NSO) fractions by silica column

chromatography, using *n*-hexane, benzene and ethanol as the solvents, respectively. *n*-Alkanes were further separated from the saturated fractions by urea-adduction and used for gas chromatography-thermal conversion-isotopic ratio mass spectrometry (GC-TC-IRMS) analyses.

Hydrogen isotopic analysis of individual *n*-alkanes was performed using the GC-TC-IRMS system at our lab (the State Key Laboratory of Organic Geochemistry, Guangzhou). An HP6890 plus GC equipped with a high temperature pyrolysis unit is interfaced via a GC-C<sub>III</sub> interface to a Finnigan Mat Delta plus<sup>XL</sup> mass spectrometer. Individual compounds as separated by using GC were pyrolysed to C and H<sub>2</sub> at 1440°C, and the latter was used to measure the hydrogen isotopic compositions.

The capillary column used for GC separation was a 60 m HP-5MS (0.32 mm × 0.25 μm). The temperature program was 60°C (isothermal for 5 min) to 290°C at 3°C/min, followed by isothermal heating at 290°C for 30 min. Ultra-high purity helium was used as carrier gas. The GC was operated in constant flow mode with a flow rate of 1.5 mL/min. All the sample injection was performed in column injection mode in order for isotopic fractionation to be completed in the injector. Typically, an amount of ~150–250 ng per compound on the column was needed to produce enough signal intensity.

The instrument was tuned to ensure that the H<sub>3</sub> factor ranges between 5–10. The H<sub>3</sub> factor was determined on a daily basis and for analyses of every 6 samples in order to ensure the stability of the mass spectrometer and the reliability of data yielded. The hydrogen isotopic compositions of individual *n*-alkanes are calibrated against the co-injected isotopic standard (provided by Indiana University) with pre-determined  $\delta D$  values. The  $\delta D$  values of the Indiana standards were measured by the conventional off-line combustion method. Typically, the  $\delta D$  values of standard compounds injected over a 24-h period did not vary by more than 2‰. Reference hydrogen gas (pre-determined and calibrated by typical IAEA SMOW/GISP/SLAP water) was also injected into the

IRMS instrument for each sample. The reproducibility and accuracy of the hydrogen isotopic analyses for unknown sample compounds were also guaranteed by the periodical injection of Indiana standards (typically one standard injection per six sample analyses).

All the samples were analyzed for more than three times but only the average values were given in this paper. All the hydrogen isotopic values were reported in the usual “‰” notation relative to VSMOW. The standard deviations for the measured samples were typically less than 5‰.

## 2 Results

Analytical results and distributions of  $\delta D$  values for individual  $n$ -alkanes of some crude oils in Lunnan Oilfield are summarized in Fig. 1. Several general observations can be made from the obtained  $\delta D$  values (Fig. 1). Apparently, hydrogen isotopic compositions of  $n$ -alkanes for three Ordovician samples from

Lunnan Oilfield and oil from Shacan 2 well are similar to those of  $n$ -alkanes for two Triassic-aged oils. The standard deviation of  $\delta D$  values for each individual  $n$ -alkanes of six samples ranges from 4.6 to 9.7, while the hydrogen isotopic ratios of  $n$ -alkanes are mainly in the range of  $-120\text{‰}$ – $-60\text{‰}$ . Moreover, hydrogen isotopic ratios tend to be increased with the increase of carbon number, in other words, lower molecular weight  $n$ -alkanes tend to show lower  $\delta D$  values than their higher homologues.

## 3 Discussions

### 3.1 Hydrogen isotopic compositions of $n$ -alkanes and its range

The hydrogen isotopic compositions of  $n$ -alkanes for crude oils in the Lunnan Oilfield are mainly in the range of  $-120\text{‰}$ – $-60\text{‰}$ . This range is similar to the range for the  $\delta D$  values ( $-117\text{‰}$ – $-97\text{‰}$ ) of Proterozoic crude oils, but largely different from that for the

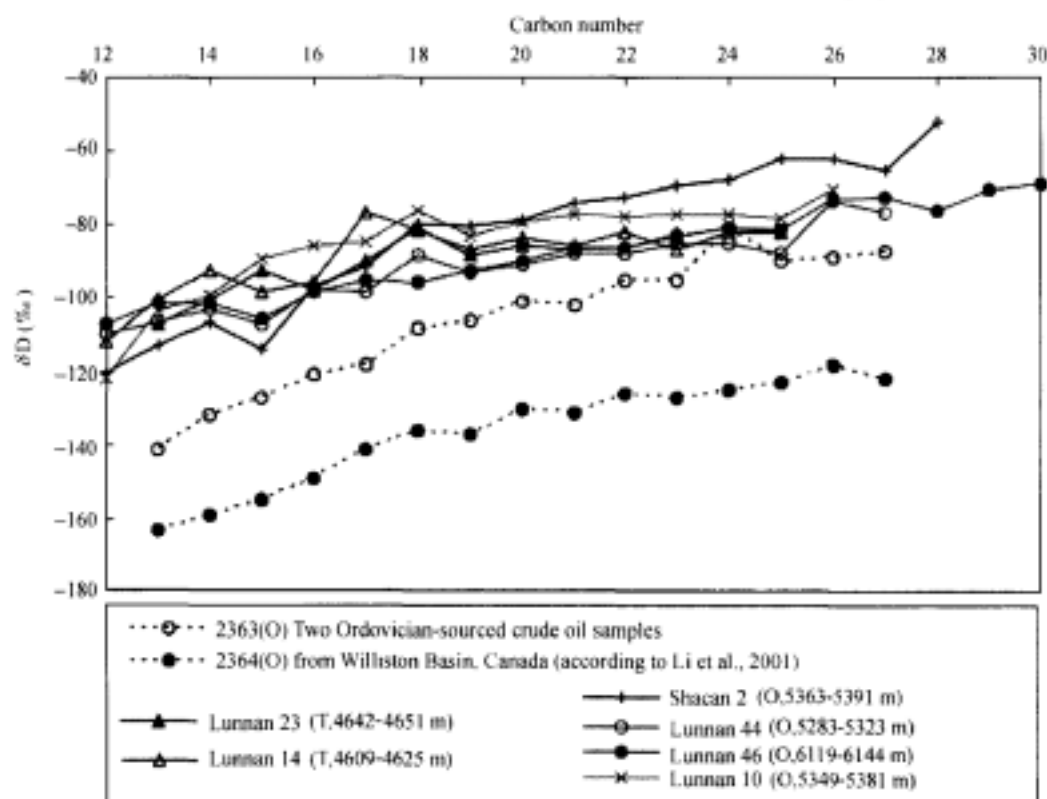


Fig. 1.  $\delta D$  values of  $n$ -alkanes for crude oils. (The hydrogen isotopic ratios measured for oils in Lunnan Oilfield, Tarim Basin, NW China are plotted in solid lines, while the data cited in dash were those for two Ordovician-sourced crude oils from Canadian Williston Basin as observed by Li et al. (2001).

$\delta D$  values ( $-187\text{‰}$ – $-105\text{‰}$ ) of Tertiary crude oils as reported by Hoering (1977)<sup>[7]</sup>. Furthermore, this range of data is similar to the range ( $-181\text{‰}$ – $-85\text{‰}$ ) for the  $\delta D$  values of the marine sourced oils as observed by Scholl (1984a)<sup>[10]</sup>, but different from the range ( $-98\text{‰}$ – $-161\text{‰}$ , with the majority between  $-137\text{‰}$  and  $-151\text{‰}$ ) for the  $\delta D$  values of the Chinese terrestrial sourced oils as observed by Fan and Claypool (1984)<sup>[11]</sup>.

Many studies have indicated that the hydrocarbons in Lunnan Oilfield are possibly derived from contributions of source rocks of Middle-Lower Precambrian and Middle-Upper Ordovician marine sediments. According to the  $\delta D$  values of *n*-alkanes in crude oils in this study, the potential source rocks seem to be mainly derived from marine sediments, which is in good agreement with the geological situation in the Tarim Basin.

The overall isotopic fractionation between environmental water and lipids biosynthesized by autotrophs is about  $147\text{‰} \pm 5\text{‰}$  in nature<sup>[16]</sup>, and about  $148\text{‰} + 4\text{‰}$  under laboratory conditions<sup>[17]</sup>. If no significant isotopic exchange is caused by secondary reactions, oils as derived from marine source rocks are more likely to have their  $\delta D$  values close to  $-150\text{‰}$ <sup>[14]</sup>, because the hydrogen isotopic composition of oceanic waters will generally be near  $0\text{‰}$ <sup>[18]</sup>. Obviously, the hydrogen isotopic compositions of individual *n*-alkanes for oils in Lunnan Oilfield have higher  $\delta D$  values. Furthermore, in comparison to the  $\delta D$  values of two Ordovician-sourced crude oils in Canadian Williston Basin as observed by Li et al. (2001)<sup>[15]</sup> (as shown in Fig. 1), the hydrogen isotopic compositions of *n*-alkanes for crude oils in Lunnan Oilfield are still characterized by higher  $\delta D$  values.

### 3.2 Curve for the distribution of the $\delta D$ values of *n*-alkanes

As shown in the curves for the distribution of the  $\delta D$  values of individual *n*-alkanes for crude oils in Lunnan Oilfield, an apparent trend can be seen that the hydrogen isotopic ratios become heavier with the increase of carbon number, which is identical to the dis-

tribution trend for oils in Canadian Basin as observed by Li et al. (2001)<sup>[15]</sup>. There is no evidence for the change of  $\delta D$  values with chain length in the *n*-alkanes, *n*-alcohols and *n*-fatty acids as isolated from a range of living organisms at present<sup>[19]</sup>. The reason for the relative enrichment of deuterium in higher molecular weight *n*-alkanes is not clear but one possible explanation could be the preferential removal of deuterium-depleted compounds. In the view point of the molecular structure, C-<sup>1</sup>H bond is preferentially existent in the product due to its relatively weak bonding energy while deuterium is held in the residual. In the thermal maturation processes of hydrocarbons, the generation velocity of lower carbon numbered *n*-alkanes is larger than that of higher carbon numbered *n*-alkanes. Correspondingly, the lower carbon numbered *n*-alkanes are deuterium-depleted while the higher carbon numbered *n*-alkanes are deuterium-enriched. This seems to be an inevitable distribution trend for *n*-alkanes.

Sufficient attention may have to be paid to this point during the study of hydrogen isotopic compositions of individual *n*-alkanes. Organic substances in nature have the largest variations in terms of the ratio of stable hydrogen isotopes simply because the two stable hydrogen isotope elements demonstrate the largest variations in terms of the relative mass number. As a result, the distribution curve of hydrogen isotopic ratios of *n*-alkanes is characterized by a slope that will be more variable than that of the distribution curve of stable carbon isotopic ratios of *n*-alkanes. According to the principle governing the slope of distribution curve resulted from the variations in generation velocity as stated above, for the distribution curve of hydrogen isotopic ratios of *n*-alkanes, the slope may contain the signal of thermal maturity of samples, while the intercept in the longitudinal axis could include the signal of source organic matter and depositional environment, if under identical conditions. Thus, the distribution curve of hydrogen isotopic ratios of *n*-alkanes can be applied to an estimate about the thermal maturity and the determination of source organic matter and depositional environment. Guan et al. (2003) used a similar method in the application of dis-

tribution model about the carbon isotopic ratios of *n*-alkanes<sup>[20]</sup>.

### 3.3 Genetic analysis about the deuterium-enriched characteristics of *n*-alkanes for Lunnan crude oils

The factors that control hydrogen isotopic ratios must be analyzed before an interpretation about the characteristics of deuterium enrichment in *n*-alkanes of oils in Lunnan Oilfield can be reasonably made. In the process of hydrocarbon generation, expulsion and migration from the original source kitchen to the present traps, the main factors that determine the  $\delta D$  values of *n*-alkanes in crude oils can be discussed as follows.

(1) Variations in source organism and depositional environment. *n*-Alkanes are mainly derived from lipids in living organisms that are biosynthesized by acetyl-CoA (pathway 1). Generally, acetyl-CoA can be originated via three pathways: (1) via the degradation of carbohydrate as resulted from photosynthesis in the chondriosome (pathway 2); (2) via the decomposition of amino acids (pathway 3); (3) via the metabolism of lipids in living organisms (pathway 4). During photosynthesis, no fractionation occurs for the hydrogen in water that was incorporated into the organism<sup>[21]</sup>, thus the  $\delta D$  values of organism are ultimately determined by the  $\delta D$  values of environmental water. Therefore, hydrogen isotopic compositions of *n*-alkanes are mainly determined by the  $\delta D$  values of environmental water and biochemical synthesis pathways of lipids (pathways 1–4). At present, it remains unknown about the variations of hydrogen isotopic compositions in the biosynthetic process of lipids. However, it can be concluded here that the hydrogen isotopic compositions of environmental water and NADPH as used in the biosynthetic reduction do have a significant influence on the  $\delta D$  values of lipid compounds. Our argument is based on several aspects listed as follows:

1) Lipids in the organism tend to be depleted in the heavy hydrogen isotopes as compared to carbohydrates and lignite. The  $\delta D$  values of some trees range from  $-34\text{‰}$  to  $-112\text{‰}$  while algae are depleted in deuterium (e.g., the  $\delta D$  values of blue-green algae are

$-107\text{‰}$ – $-147\text{‰}$ ). *n*-Alkyl lipids are depleted in deuterium relative to growth water by  $113\text{‰}$ – $262\text{‰}$ , while polyisoprenoid lipids are depleted in deuterium relative to growth water by  $142\text{‰}$ – $376\text{‰}$ <sup>[19]</sup>.

2) Water is the main source of hydrogen used by primary producers<sup>[22,23]</sup>. The  $\delta D$  values of water will be enhanced with the increase of salinity due to preferential evaporation of  $^1\text{H}_2\text{O}$  than  $\text{D}_2\text{O}$ . As a result, terrestrial fresh water is depleted in deuterium ( $\delta D = -2\text{‰}$ – $-90\text{‰}$ ) while salt sea water is enriched in deuterium ( $\delta D = -20\text{‰}$ – $0\text{‰}$ ). Correspondingly, the stable hydrogen isotopic compositions of marine oils range from  $-85\text{‰}$  to  $-181\text{‰}$  while nonmarine oils have  $\delta D$  values ranging between  $-130\text{‰}$  and  $-163\text{‰}$ <sup>[10]</sup>. Generally speaking, if the environmental conditions are identical, the enrichment of  $\delta D$  values of waters can generally be related to paleoenvironments characterized by warm and semiarid to arid climates, simply because intense evaporation of water can result in the subsequent enhancement of deuterium concentration in liquid phase<sup>[24,25]</sup>. The trend of enrichment of  $\delta D$  values for kerogens and crude oils under saline depositional conditions has been verified by many studies<sup>[11,26–28]</sup>. The highly reductive and salted depositional environment for marine source rocks in the Tarim Basin, NW China, which inevitably produce enriched  $\delta D$  values for individual hydrocarbons, has been validated by abundant gammacerane and aryl isoprenoids detected in the source rocks and crude oils<sup>[29]</sup>.

(2) Effect of thermal maturation on  $\delta D$  values. When the maturity of the oils changes from marginally mature to highly mature, a  $40\text{‰}$  enrichment was observed by Li et al. (2001)<sup>[15]</sup> in the weighted average  $\delta D$  values of *n*-alkanes in the oils from Canadian Sedimentary Basin. A similar trend towards less negative  $\delta D$  values with increasing thermal maturity was also observed in source rock kerogens in the Mahakam Delta<sup>[30]</sup>, the Norwegian North Sea<sup>[31]</sup> and the coal extracts from Australia<sup>[5]</sup>. Generally, the increase of thermal maturity of crude oils will result in the enhancement of the slope of the curve.

(3) Effect of migration on  $\delta D$  values. Although it remains unknown as to the isotopic fractionation effect during oil migration from the original source kitchen to the present traps, no evidence has been found so far that significant hydrogen isotopic exchange occurs during secondary migration and progressive vaporization of crude oils<sup>[14]</sup>. In the studies about hydrogen isotopes of individual *n*-alkanes in Canadian Williston Basin by Li et al. (2001)<sup>[15]</sup>, only a small variation (4‰) was observed in the weighted average  $\delta D$  values of the  $C_{12}$ – $C_{27}$  *n*-alkanes for those oils with a lateral migration distance of at least 150 km. In this study, Lunnan 46 well is located in the west side of the Jiefangqu-Jilake tectonic zone, Lunnan 14, Lunnan 23 and Lunnan 44 wells are located in the east, middle and west parts of the Sangtamu faulted zone, respectively, while Lunnan 10 well is located in the east part of the Lunnan faulted zone. However, no systematic variation of hydrogen isotopic ratios of *n*-alkanes in large magnitude exists for these crude oils, which suggests that little interaction among the hydrogen isotopes occurs between migrating oil and the carrier rocks.

(4) Hydrogen isotopic exchange reaction. Possible hydrogen isotopic exchange must be taken into account at the late diagenetic stage owing to the enhancement of thermal stress. However, hydrogen element in the organic matter is linked by C-H bond with higher bond-energy. As a result,  $H_2O$  at neutral pH and low temperature in the absence of a catalyst does not readily exchange with most carbon-bound organic hydrogen. Thus, significant hydrogen isotopic exchanges between *n*-alkanes in crude oils and sedimentary water are unlikely to occur under typical reservoir conditions over geological time<sup>[15]</sup>. Furthermore, results of long-duration experiments as performed by Yeh and Epstein (1981), who heated a mixture of oil and D-enriched water ( $\delta D = 2000‰$ ) at  $180 \pm 20^\circ C$  for two months, show that exchange of hydrogen isotopes between the oils and water is not extensive enough to affect the  $\delta D$  values of crude oils<sup>[9]</sup>. In Fig.1, the large variations of stable hydrogen isotopic compositions for *n*-alkanes with different carbon numbers, reveal no exchange of stable hydrogen isotopes in Lunnan crude

oils.

On the basis of analyses of factors that control hydrogen isotopic ratios, it is reasonable to conclude here that, with the premise of similar algae sources and identical oceanic biochemical settings, the deuterium enrichment in *n*-alkanes for oils in Lunnan Oilfield mainly reflects the salinity environment during sedimentation of source organic matter. The consistent slope of the distribution curves indicates that these oils are at a similar thermal maturity stage. The similarity in distribution curves for oils from different aged reservoirs is indicative of the similarity of depositional water environments.

#### 4 Conclusions

We have measured the hydrogen isotopic compositions of individual *n*-alkanes for several typical crude oils from Lunnan Oilfield, Tarim Basin, NW China by using the newly developed gas chromatography-thermal conversion-isotope ratio mass spectrometry. The similar range of  $\delta D$  of individual *n*-alkanes for crude oils among reservoirs with different geological times reflects that hydrocarbons are all derived from the same marine depositional environment. Compared to the theoretic value ( $-150‰$ ) and the reported  $\delta D$  values ( $C_{12}$ – $C_{27}$ ,  $-160‰$ – $-90‰$ ) of individual *n*-alkanes for Ordovician-sourced crude oils in Canadian Williston Basin, the hydrogen isotopic composition of individual *n*-alkanes in crude oils from Lunnan Oilfield is characterized by heavy hydrogen isotopic values ( $C_{12}$ – $C_{27}$ ,  $-120‰$ – $-60‰$ ). Based on the analyses of the factors that control hydrogen isotopic values during generation and thermal maturation, the higher  $\delta D$  values of individual *n*-alkanes in crude oils from Lunnan Oilfield, Tarim Basin, NW China, can be related to the relatively saline depositional environment and the higher thermal maturation stage.

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