H and C isotope trends and anomalies
in hot and mature oils from the Pannonian Basin

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Crude oil samples from uncommonly hot (>170°C) reservoirs of the SE-Pannonian Basin were studied for stable carbon and hydrogen isotope compositions of their different fractions. From two fields, 15 samples of different depths and temperatures were chosen for this study. The aim was to study the impact of extreme reservoir conditions on the isotope ratios of the different fractions and to find the ratios that show correlation with increasing depth and temperature.

We have shown that the behaviour of isotopes in these very hot oils differs from those from lower temperatures. The combined application of carbon and hydrogen isotope techniques is useful and may provide approximate information on reservoir conditions.

Key words: crude oil, oil fractions, δD, δ^{13}C, hot reservoirs

Introduction

Stable isotope ratios have always been among the best tools of organic geochemists studying oil generation, migration, maturation, oil-to-oil and oil-to-source rock correlation. The stable isotopic compositions of crude oil fractions (e.g. saturated, aliphatic, aromatic etc.) are proven to be very informative and useful techniques and so are the isotope type-curves (e.g. Galimov 1973; Stahl 1978). The application of D/H ratios is also a well-known tool in determining the source, maturity and biodegradation of crude oils. The use of isotopic compositions of oil fractions is a reliable isotope technique.

Oil traces of the Makó–Hódmezővásárhely-trough (M–H-trough), Pannonian Basin have been studied recently (Fekete et al. 2009, 2010, 2011). The isotope type-curves formed from the stable carbon and hydrogen isotope compositions of different oil fractions were found to be good tools to group these oils of different origins. However, the carbon and hydrogen stable isotopic compositions of fractions in these oils are not obvious.

In this paper we study the stable carbon and hydrogen isotope ratios in different fractions of very hot oils from two sites from the M–H-trough. Ten of the fifteen samples was investigated former (Fekete et al. 2011). Our aim is to present the isotopic features of high temperature oils (from 170°C to 215°C) and we also try to briefly interpret the effects of the extreme reservoir conditions.

Geological setting and samples

The M–H-trough is one of the deepest subbasins of the Pannonian Basin. It is filled with Neogene and Quaternary sediments (silts, fine grained marls, calcareous marls, sandstones and shales of brackish and lacustrine environments) up to the thickness of 7000 meters. However, giant Algyő oil and gas field is located adjacent to the area, up to now, identification of proven source rocks has been unsuccessful; candidates are shales from the basal part of the basin fill (Koncz et al. 1999). The geothermal gradient is varying around 40°C/km depending on depth (Dövényi and Horváth 1988; Sajgó 1980; 2000; Sajgó et al. 1988; Hetényi et al. 1993).

Samples were chosen from four (SI1; SI2-3; SII; SI4–9) wells of two fields close to each other and located in the M–H-trough. For proprietary reasons the names of the wells and fields are changed and also the exact depth and temperature values are not presented. "SI" and "SII" represent the two sites and increasing numbers represent the increasing depths and temperatures. The oils are mature or very mature ones and show no signs of biodegradation (Sajgó 2000). SI4 and SII1 are so-called "kick" samples that were taken when the drill reached the first oil reservoir. These samples can be contaminated by the drilling mud and the formation waters.

Sample preparation and methods

The oil samples are 'topped' oils not containing any <C14 compounds.

Separation of oil fractions was carried out on the basis of the method used by Sajgó (1980). The fractions and their abbreviations (between brackets) are as follows: n-alkanes (n-alk), saturated aliphatic (sat), n-alkane-free saturated (isoalkanes, in our case predominantly isoprenoid alkanes; iso), aromatic hydrocarbon (aro) fraction, resin (heteroaromatic) compounds (NSO), asphaltenes (asph).

The samples were oxidized with copper-oxide in evacuated and flame-sealed pyrex tubes at 480°C based on the method of Sofer (1980). The evolved H_2O and CO_2 were separated by means of vacuum distillation using liquid nitrogen and ethyl-alcohol cooled below –80 °C. H_2 gas was produced from H_2O using the zinc reduction method (Coleman et al. 1982; Demény 1995).

The D/H and $^{13}C/^{12}C$ ratios were determined using a Finnigan MAT delta S mass spectrometer. The results are given in the conventional δ value (δ = $(R_{sample}/R_{standard})*1000$, where Rsample and Rstandard are the D/H and $^{13}C/^{12}C$ ratios in the sample and standard, respectively) relative to V-SMOW (H) and V-PDB (C) in ‰. Based on sample reproducibility and differences in δD and $δ^{13}C$ values obtained for standards from their theoretical values, the results are accurate at ±3‰ for δD and better than ±0.1‰ for $δ^{13}C$. See Fekete et al. (2011) for detailed description.

Results and discussion

The carbon isotopic composition of oils is basically determined by the composition of the original organic matter (i.e. contribution of different biota: higher plants to algae), salinity of the depositing water body and climate. During deposition and burial, diagenesis and maturation processes the carbon isotopic composition may change (Galimov 2006). It can be greatly changed by biodegradation and partly by maturation processes but is assumed to remain constant during migration. Maturation causes saturated fraction to be enriched and asphaltenes (and NSO compounds) to become depleted in ^{13}C (Galimov 2006). Aromatic hydrocarbons are the most resistant fractions to isotope change (Stahl 1980; Schoell 1984).

The D/H ratio of oil is determined by the hydrogen isotope compositions of the initial organic matter and that of the formation water at the time of deposition and the subsequent rock-water-oil interactions at high temperatures during migration or in the reservoir rocks. The oils may become enriched in D due to their interaction with formation waters, as suggested by pyrolysis experiments (Schimmelmann et al. 2001). The hydrogen exchange with water mainly affects the NSO compounds and mildly other aromatics.

Our results are listed in Table 1. $^{13}C/^{12}C$ and D/H ratios of the fractions are presented in aliphatic and non-aliphatic separate plots (Figures 1–4). $δD_{aro}/δD_{NSO}$ and $δD_{asph}/δD_{NSO}$ ratios are plotted in Figure 5.

The $δ^{13}C$ values of n-alkanes slightly decrease and those of isoalkanes increase in the middle sample set (SII), while that of the saturated fraction does not show a definite trend. The least hot and the hottest samples of the other sample set (SI) do not show any obvious trend. The $δ^{13}C$ of the saturated fraction varies slightly between –27.8 and 27.0‰ with one extremely high value of –25.5‰ (Figure 1). The isoalkanes are distinctively enriched in ^{13}C compared to n-alkanes, the SI5

sample excepted. Bjoroy et al. (1991) also reported that isoprenoids were generally heavier than n-alkanes in oils.

The $\delta^{13}C$ values of the three non-aliphatic fractions (Figure 2) do not show any significant trend. The values are more scattered than those of aliphatic fractions. Asphaltene $\delta^{13}C$ values show the largest variability with two outliers (SI3 and SI9) which shows the instability of this fraction. The $\delta^{13}C_{aro}$ is generally 1–2‰ less negative than $\delta^{13}C_{NSO}$ and $\delta^{13}C_{asph}$. This is the effect of maturation (Galimov 2006). Similar phenomenon was found by e.g. Cortes et al (2010). The two "kick" samples do not show regular deviation; however, SII1 $\delta^{13}C_{NSO}$ and $\delta^{13}C_{asph}$ values are more negative compared to those of SII2–SII6.

The δD of aliphatic fractions vary in a relatively narrow range of –135 – –115‰ (Fig. 3) and shows a slight increase towards greater depths and temperatures. It is notable that δD of isoalkanes is the same or somewhat less negative than that of n-alkanes in the first (SI1–SI3) group, and in the others (SII and SI4 – SI9) n-alkanes are enriched in D compared to isoalkanes. In SII the correlation is good between δD_{n-alk} and δD_{iso}, and exists in SI.

Relationship between hydrogen isotopic compositions of non-aliphatic fractions is rather complicated (Fig. 4). The values are scattered between ~–90 and –160‰. We can observe that with one exception the δD values of aromatic and asphaltene fractions run close to each other, and that of NSO compounds is far more negative. The δD_{aro} and δD_{asph} decrease and δD_{NSO} increases with increasing depths and temperatures in SI. In SII this phenomenon cannot be observed.

$\delta D_{aro}/\delta D_{NSO}$ and $\delta D_{asph}/\delta D_{NSO}$ increase in both groups (Fig. 5). As stated former, the NSO compounds are the most affected by hydrogen exchange processes, but this increase in the mentioned values is unexpected. As Figures 4 and 5 show, "kick" samples are exceptions, because their NSO compounds are enriched in D.

On the basis of the results discussed former we can state the following:

1. The $\delta^{13}C$ of the isoalkane fraction is less negative than that of the n-alkanes. The extreme high temperature has not affected the general difference between the two fractions. At high temperatures the non-aliphatic fractions are not resistant to isotope fractionation and their δ values are more variable. The $\delta^{13}C$ of aromatic fraction is 1–2‰ less negative than that of asphaltene and NSO compounds.

2. The δD of aliphatic fractions is less variable than that of non-aliphatic fractions. A slight enrichment of D may be observed in the fractions towards greater depths and temperatures, but δD values do not show strong temperature dependence. Aromatic and asphaltene fractions represent the least negative δD values, and in negative direction n-alkanes, isoalkanes and NSO compounds follow, which are strongly depleted in D. In one sample set (SII) the $\delta^{13}C_{n-alk}$ decreases and $\delta^{13}C_{iso}$ increases with increasing depth and temperature, in the

other (SI) δD_{aro} and δD_{asph} decrease and D_{NSO} increases with increasing depths and temperature.

3. In high temperature reservoirs the application of carbon and hydrogen stable isotopes is limited. The inherited isotopic features were partly preserved in the oils, and the temperature dependent isotopic trends are exhibited clearly only by oils of the same organic facies.

4. Our results corroborate the observation, that NSO compounds are the most affected by hydrogen exchange processes. The samples studied show the relative deuterium depletion of NSO fraction.

5. "Kick" samples differ from the others mainly in their increased δD_{NSO} values. A contamination effect is not excluded.

Table 1
C and H stable isotopic compositions of the oil fractions

Sample	$\delta^{13}C$ (‰)						δD (‰)					
	n–alk	sat	iso	aro	NSO	asph	*n*–alk	sat	iso	aro	NSO	asph
SI 1	−27.9	−27.3	−26.3	−25.9	−27.5	−26.7	−117	−118	−121	−106	−149	−105
SI 2	−27.8	−27.2	−26.0	−25.6	−28.3	−27.6	−130	−127	−120	−116	−142	−114
SI 3	−27.8	−27.4	−26.5	−26.0	−27.1	−23.3	−124	−124	−127	−121	−147	−116
SII 1	−28.0	−27.3	−26.5	−26.3	−29.8	−29.5	−128	−130	−133	−105	−119	−110
SII 2	−28.0	−27.4	−26.6	−25.1	−27.8	−27.4	−124	−124	−123	−103	−149	−109
SII 3	−28.1	−27.4	−26.5	−26.0	−27.2	−27.5	−119	−121	−124	−100	−157	−125
SII 4	−28.3	−27.3	−26.4	−25.4	−27.4	−27.1	−122	−125	−128	−97	−144	−102
SII 5	−28.2	−27.3	−26.5	−25.4	−27.2	−28.1	−119	−122	−124	−102	−138	−104
SII 6	−28.5	−27.6	−26.3	−25.3	−26.7	−27.2	−128	−126	−121	−127	−152	−125
SI 4	−28.3	−27.8	−26.9	−27.4	−28.5	−28.4	−124	−124	−122	−101	−100	−90
SI 5	−25.5	−25.5	−25.4	−26.2	−26.8	−27.8	−116	−116	−115	−98	−140	−101
SI 6	−28.2	−27.4	−26.3	−26.1	−28.4	−27.6	−116	−118	−122	−108	−134	−101
SI 7	−27.0	−27.0	−26.7	−26.8	−28.0	−27.7	−116	−116	−119	−103	−127	−102
SI 8	−27.3	−27.1	−26.5	−25.6	−27.8	−28.0	−121	−121	−121	−101	−126	−109
SI 9	−27.6	−27.2	−26.4	−26.2	−27.9	−25.6	−119	−120	−123	−117	−129	−117

6. Crude oils from similar depths and adjacent localities have shown different isotopic behaviour. The reason for this may be the different heritage of the oils (^{13}C) and the different hydrogeological conditions (D).

Conclusions

This study has demonstrated that the combined application of $\delta^{13}C$ and δD data of different fractions is useful and may carry information on relative reservoir conditions and crude oil relationships; however, the interpretation of
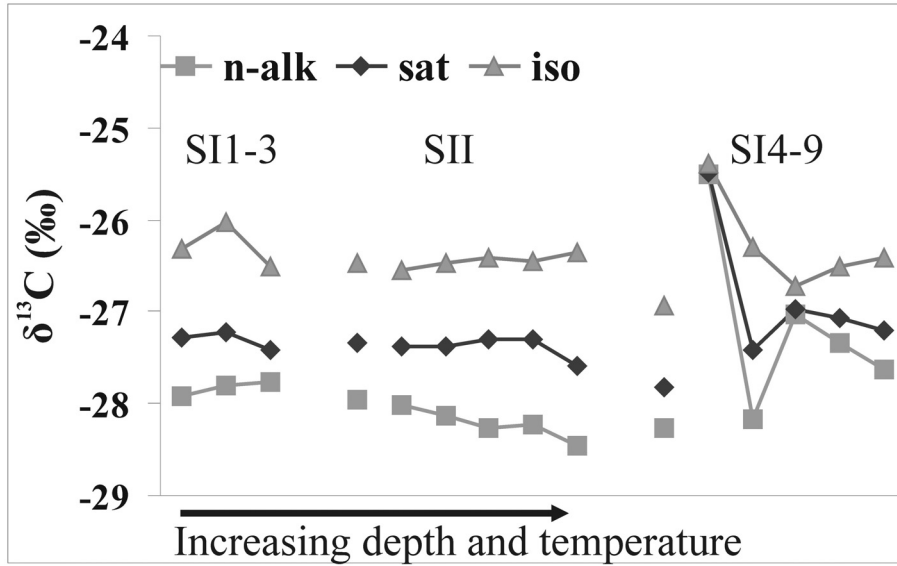
Fig. 1
δ¹³C of the aliphatic fractions

Fig. 2
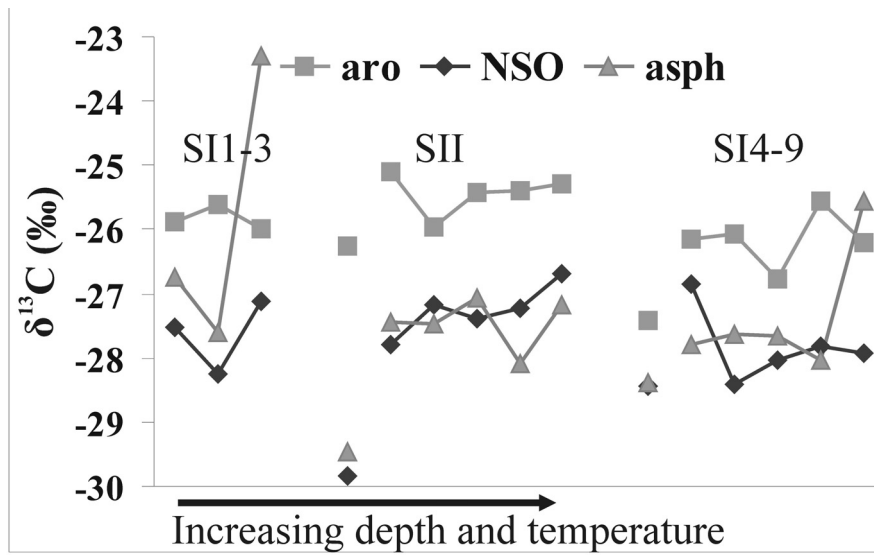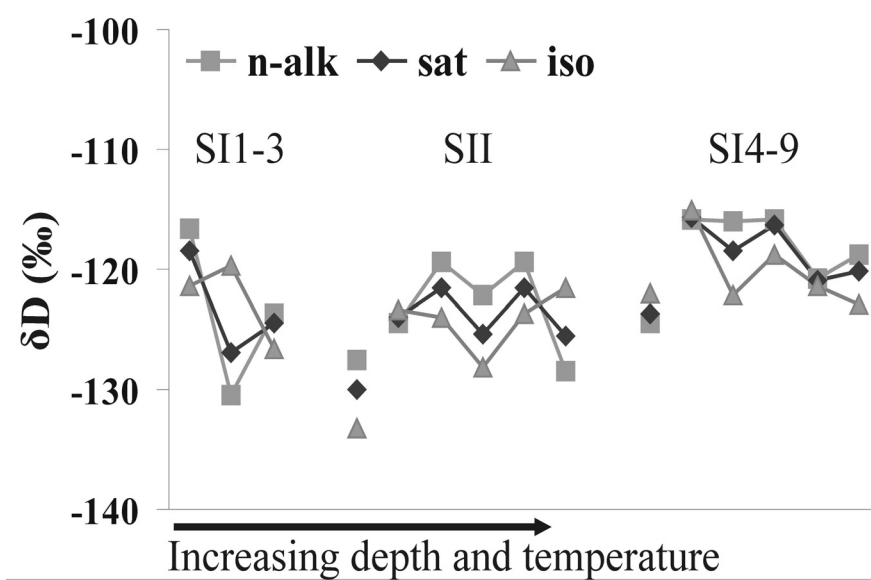δ¹³C of the non-aliphatic fractions
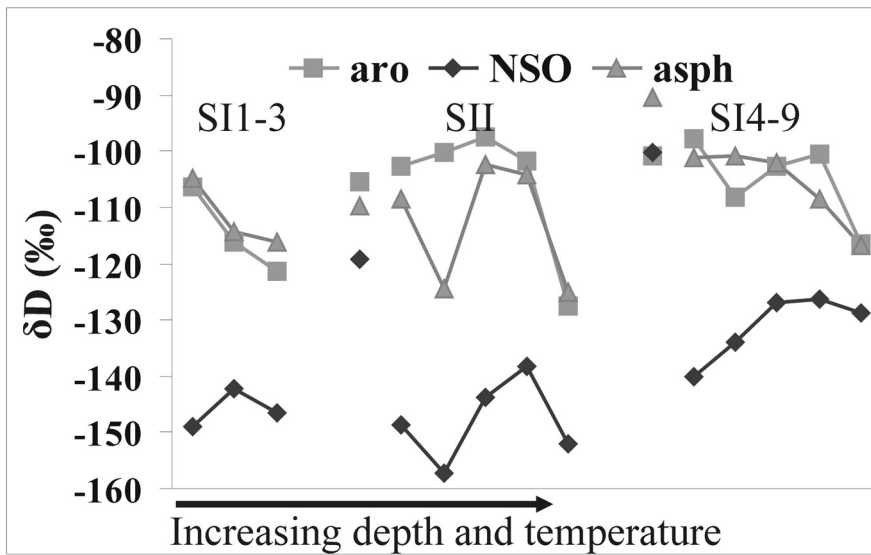
Fig. 3
δD of the aliphatic fractions
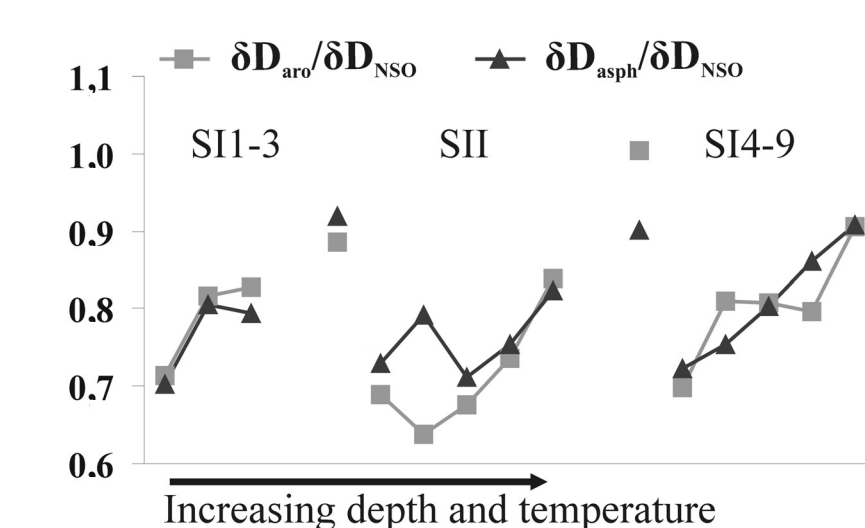

Fig. 4
δD of the non-aliphatic fractions

Fig. 5
δD ratios of the non-aliphatic fractions

carbon and hydrogen isotope ratios is rather complicated in very hot and mature crude oils. In the case of some fractions trends can be observed: the inherited isotopic composition is slightly overprinted by the effect of temperature.

Acknowledgements

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