

Applications of Aromatic Hydrocarbons to Assess Thermal Maturity and Families of Termit Basin Oils, Niger

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Abstract. A suite of 23 crude oil samples from the Termit Basin, Niger, were analyzed for geochemical characterization of thermal maturity and family classification. Distribution of alkylnaphthalenes, alkyl phenanthrenes, triaromatic steroids and aromatic biomarkers were reported from aromatic fractions of these oils. Oil-oil correlation suggests that these oils in Termit basin show two typical different geochemical characteristics, and can be divided into two different groups, and most of the oils belongs to family I. Methyl triaromatic steroids, and relatively higher abundance of triaromatic dinosteroids in these oils from Family I indicate a characteristics of crude oils of marine origin. Methyl triaromatic steroids and triaromatic dinosteroids were detected in the oils from Family II, and triaromatic dinosteroids are present in lower abundance relatively to methyl triaromatic steroids. The maturity values calculated by the methyl phenanthrene index (MPI-1) and trimethyl naphthalene ratio 2 (TNR-2) suggest that these oils most probably were generated by source rocks with the maturation stage of 0.6% to 1.0% (Ro). The oils from the Family II appear to have relatively higher maturity. This is the first study to report the distribution of aromatic hydrocarbons from the Termit Basin crude oils. The identification of family II in this basin can further improve the hydrocarbon play concept as well as provide new insights of hydrocarbon exploration with the Basin.

Keywords: Aromatic hydrocarbon \cdot Thermal maturity \cdot Oil family \cdot Termit basin · Niger

1 Introduction

The Termit Basin, eastern Republic of Niger (see Fig. [1\)](#page-1-0) has an area of 27000 km^2 . The basin is a Mesozoic-Cenozoic rift belong to the West and Central African Rift System (WCARS) [\[1](#page-6-0)–[3](#page-6-0)]. Many discoveries have been made in the Termit Basin, since the first well was drilled in 1974.

The Upper Cretaceous Yogou Formation source rocks contain good to excellent source rocks which have been assumed to be the potential source rocks in the Termit basin [\[4](#page-6-0)]. Sixty Paleogene and sixteen Upper Cretaceous oils were analyzed based on saturated hydrocarbon distributions and stable carbon isotopic compositions [[5\]](#page-6-0). However, the detailed aromatic hydrocarbon characteristics and their application in assessment of maturity and families for these oils from the Termit Basin have not yet been studied and geochemical studies related to the basin are relatively few.

Biomarker distributions of aromatic hydrocarbon fractions were studied in order to investigate the thermal maturity and family classification.

Fig. 1. Regional map of the WCARS and the location of the Termit Basin

2 Materials and Methods

23 oils samples, selected from the Sokor1 and Yogou Formation in the Termit Basin, were analyzed in this study. Figure 2 shows the locations of the sampled wells.

Fig. 2. Map of the Agadem Block in the Termit Basin. The studied oils are sampled from these wells showing in the map.

The sample preparation, liquid chromatography and GC-MS were performed similar to those described in Wan et al. (2014). Briefly, we used liquid chromatography with silica gel/alumina columns to fractionate saturated and aromatic hydrocarbon fractions, which were eluted by n-hexane with dichloromethane $(50:50, v:v)$ and dichloromethane, respectively. The aromatic fractions were carried out using an Agilent 5975i GC-MS system fitted with an HP-5 MS fused silica capillary column. The GC operating conditions are similar to those described in performed Wan et al. (2014). Briefly, the starting temperature of oven was 50 $^{\circ}$ C, reaching a temperature of 120 °C by a ramp of 20 °C/min, then reaching a final temperature of 310 °C at 3 ºC/min, and holding for 25 min. For the aromatic fractions, the starting temperature was 80 °C for 1 min, ramped to 310 °C at 3 °C/min, and then held for 16 min.

3 The Compositions of Aromatic Hydrocarbons

3.1 Triaromatic Dinosteroids and Methyl-Triaromatic Steroids

It is reported that the precursors of dinosteranes and triaromatic dinosteroids are dinosterols and related sterols in modern marine dinoflagellates [[8,](#page-6-0) [9](#page-6-0)]. Dinosteranes and triaromatic dinosteroids are related to ancient dinoflagellates $[7-10]$ $[7-10]$ $[7-10]$ $[7-10]$. Abundant triaromatic methyl-triaromatic steroids and triaromatic dinosteroids were detected in Termit Basin oils by conventional GC-MS analyses (see Fig. 3).

Fig. 3. Representative m/z 245 mass fragmentograms showing the distribution of methyltriaromatic steroids and triaromatic dinosleranes in Termit Basin oils. Note: The compounds in the figure with ▼ is triaromatic dinosteroids; 4- and 3- is 4-methyl triaromatic steroids, 3-methyl triaromatic steroids, respectively.

The high concentration of triaromatic dinosteroids and methyl-triaromatic steroids in most of the oils from the Termit Basin indicates their affinity in source of oils. While the crude oils of wells DD-2 (2101.3–2113 m), D-1 (2108.4–2114.7 m) and Tr-1(2680.2– 2694.1 m) are predominated by methyl-triaromatic steroids, and the abundance of triaromatic dinosteroids is relatively much lower (see Fig. [3](#page-2-0)). Previous studies indicated that the triaromatic dinosteroids and methyl-triaromatic steroids are detected in the organic matter of marine origin or related petroleum $[7-10]$ $[7-10]$ $[7-10]$ $[7-10]$ $[7-10]$. However, the organic matter of lacustrine origin and related oils are dominated by 4-methyl triaromatic steroids. Therefore, most of oil samples in the Termit Basin are of marine origin, whereas the oils of wells DD-2 (2101.3–2113 m), D-1 (2108.4–2114.7 m) and Tr-1 (2680.2– 2694.1 m) are generated from organic matter deposited in lacustrine environment.

3.2 Triaromatic Steroids (TAS)

TAS are considered to be evolved from monoaromatic steroids [\[10](#page-6-0)–[12](#page-6-0)]. The distribution of C_{26} , C_{27} , C_{28} triaromatic steroids can be used as oil-source correlation [[13](#page-6-0)– [15\]](#page-6-0). The C_{26}/C_{28} 20S and C_{27}/C_{28} 20R triaromatic steroid ratios are useful parameters to understand different petroleum systems.

Compared with regular steranes, TAS miss one methyl in C-10 and C_{13} , while adding one in C-17, so it causes steric hindrance during the isomerization in C-20, so TAS C-20 isomerization maturity value is more efficient in the high maturity light oil and Condensate crude oil.

Figure 4 shows the TAS distribution in Termit Basin oils. Most of the oils have relatively low concentrations of C_{26} 20S, C_{26} 20R + C_{27} 20S and C_{27} 20R triaromatic

Fig. 4. Representative m/z 231 mass fragmen to grams showing the distribution of triaromatic steroids in Termit Basin oils.

steroids, in contrast to the oils from well DD-2 (2101.3-2113m), D-1 (2108.4– 2114.7 m) and Tr-1(2680.2–2694.1 m).

4 Results

4.1 Oil Family Classification

The oil-oil correlation suggests that the Termit basin oils can be divided into two oil compositional families.

The majority of the oils belongs to group I. This study discovered that methyl triaromatic steroids, and relatively higher abundance of triaromatic dinosteroids in group I oils, which showed a characteristics of crude oils of marine origin. Triaromatic steroids are characterized by low C₂₇20R and C₂₆20S (C₂₇/C₂₈ 20R < 0.35, C₂₆/C₂₈ $20S < 0.20$).

Methyl triaromatic steroids and triaromatic dinosteroids were detected in the Group II oils, and triaromatic dinosteroids are present in lower abundance relatively to methyl triaromatic steroids. The oils of this group is characterized by higher $C_{27}20R$ and C_{26} 20S triaromatic steroid isomers $(C_{27}/C_{28}$ 20R > 0.35, C_{26}/C_{28} 20S > 0.20). By current, oils of group II include three crude oil samples, well DD-2 (2101.3–2113 m), D-1 (2108.4–2114.7 m) and Tr-1(2680.2–2694.1 m).

The cross plot of C_{27}/C_{28} 20R TAS $-C_{26}/C_{28}$ 20S TAS shows the Termit basin oils can be divided into two oil families (see Fig. 5). Most of the oils have lower values of C_{27}/C_{28} 20R triaromatic steroids and C_{26}/C_{28} 20S triaromatic steroids and can be classified as one type. The oils from well DD-2 (2101.3–2113 m), D-1 (2108.4– 2114.7 m) and Tr-1 (2680.2–2694.1 m) have relatively higher parameter values and can be classified as another family.

Fig. 5. C_{27}/C_{28} 20R TAS versus C_{26}/C_{28} 20S TAS indicating two oil families for the Termit Basin oils.

This is the first study to report the distribution of aromatic hydrocarbons from the Termit Basin crude oils. The identification of family II in this basin can further improve the hydrocarbon play concept as well as provide new insights of hydrocarbon exploration with the Basin.

4.2 Maturity Assessment

Parameters based on aromatic hydrocarbons are effective for thermal maturity evaluation. The methyl phenanthrene index (MPI-1) is useful to estimate vitrinite reflectance [\[16](#page-7-0)]. Several parameters related to trimethyl naphthalene were also proposed to evaluate the thermal maturity of oils. The trimethyl naphthalene ratio 1 (TNR-1) is equal to the 2,3,6-TMN to the sum of 1,4,6- and 1,3,5-TMN, and The trimethyl naphthalene ratio 2 (TNR-2) is equal to the ratio of 1,3,7- and 2,3,6-TMN to the sum of 1,4,6-, 1,3,6- and 1,3,5-TMN [[17,](#page-7-0) [18\]](#page-7-0).

On the basis of measured Ro%, the equation TNR-2 and calculated Rc% wer proposed, i.e. $\text{Rc\%} = 0.4 + 0.6 \times \text{TNR-2}$.

Figure 6 illustrated the approximate maturation levels on the basis of calculated vitrinite reflectance. In general, the crude oil in Termit basin was generated by source rocks with the maturation stage of 0.6% to 1.0% (Ro). The oils in group II appear to have relatively higher maturity.

Fig. 6. Plot of hopane maturity parameters between calculated vitrinite reflectance from Rcb (TNR-2) and Rca (MPI-1).

5 Conclusions

The distribution of aromatic hydrocarbons indicates that the Termit basin oils show two typical different geochemical characteristics, and can be classified as two oil families, and the most of oils belongs to family I. The oils of family I are characterized by

relatively higher abundance of triaromatic dinosteroids, low abundance of C_{27} 20R and C_{26} 20S Triaromatic steroids.

The maturity values calculated by the MPI-1 and TNR-2 suggest that source rocks of Termit basin oils are at the maturation stage of 0.6% to 1.0% (Ro). The oils from the Family II appear to have relatively higher maturity.

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