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# Research paper

# Bicyclic alkanes in source rocks of the Triassic Yanchang Formation in the Ordos Basin and their inconsistency in oil-source correlation



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## ABSTRACT

The Triassic Yanchang Formation is the main source rocks for Mesozoic oil in Ordos Basin. The formation includes 10 oil-bearing beds (Ch 1-Ch 10), that each can be further divided into two to three intervals. Abundant C<sub>12</sub>-C<sub>14</sub> and C<sub>15</sub>-C<sub>16</sub> bicyclic alkanes have been detected in the formation in the Xifeng oilfield, Ordos Basin. The  $C_{12}-C_{14}$  group is dominated by  $C_{12}$  and  $C_{13}$ , and the  $C_{15}-C_{16}$  group contains abundant  $C_{15}$ . The groups show three distribution patterns: A) the  $C_{12}-C_{14}$  group is the major component in the non-source rocks of the Ch 7-1 and Ch 8-1 intervals; B) both groups are abundant and are common in source rocks of the Ch 7-3 interval; and C) the  $C_{15}-C_{16}$  group is the major component in source rocks of the Ch 7-3 interval and also in sediments that contain type I or partial sapropel type II<sub>1</sub> organic matter (OM) in the Ch 7-2 and Ch 8-1 intervals. Although thermal maturities of the source rocks in the Ch 7 section are similar, they show significant differences with respect to the drimane isomerisation index, which indicates that the drimane rearrangement is controlled by thermal evolution of the sediments, but may also be closely related to the depositional environment. This study determined that reducing environments are more conducive to preservation of drimane than oxic environments. The drimane isomerisation index and the value of the hopane parameter Tm/Ts are positively correlated. The parameter Tm/Ts varies over a wide range within the sequence, and the large variations may be a result of terrigenous OM input by turbidity currents and/or gravity flows, mixed with the autochthonous sediments. Abundant homodrimane in both source rocks may reflect reducing environments in deep lakes and major input of higher plant OM. Organic-rich shale and oil shale in the Ch 7-3 interval of the Yanchang Formation are the primary sources of oil in reservoirs in the Xifeng area. The crude oil is rich in bicyclic alkanes that are dominated by  $C_{15}-C_{16}$  as source rocks with pattern C for bicyclic alkanes, which indicates an origin mainly from the Ch 7-3 interval. The main peaks in all of the crude oils are associated with  $8\beta(H)$ -drimane and lower abundance of rearranged drimane. However, most of the source rocks have a main peak associated with  $8\beta(H)$ -homodrimane or rearranged drimane. Weak microbial action, selective degradation and water washing may be the cause of the significant difference in bicyclic sesquiterpane composition between the crude oil and the source rocks. The result suggests that oil-source correlations based on the bicyclic sesquiterpanes are questionable.

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## 1. Introduction

Bicyclic alkanes and bicyclic sesquiterpanes are widely distributed in a variety of sediments and crude oil, but their compositions and distributions differ. Philp et al. (1981) first reported the

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http://dx.doi.org/10.1016/j.marpetgeo.2016.02.021 0264-8172/© 2016 Elsevier Ltd. All rights reserved. discovery of bicyclic alkanes in non-marine crude oils of different ages in Australia and interpreted them as products of different levels of bacterial degradation. A series of single unsaturated tricyclic diterpenes ( $C_{20}H_{34}$ ) detected in the crude oil was thought to be the source. The authors concluded that  $8\beta(H)$ -drimane is synthesised from drimenol and may have a bacterial origin.  $4\beta(H)$ eudesmane oil with a  $C_{15}$  bicyclic structure is a typical marker of higher plants that are derived from  $\beta$ -eudesmol plant components. Alexander et al. (1983, 1984) suggest that bicyclic alkanes are bacterial metabolic products that form during early diagenesis from degraded bacterial hopanes by ring opening. Many types of isomeric bicyclic alkanes form during late diagenesis by the removal and rearrangement of functional groups. The  $C_{14}$ – $C_{16}$ drimane series is usually derived from bacteria and other microbes.  $8\beta(H)$ – $C_{20}$  homodrimane has been found in algal coal, which indicates that the  $8\beta(H)$ -drimane series may have a variety of precursors, including bacteria, algae, tricyclic terpanes with long side chains, and the derivatives of 8, 14-secohopane and hopane series by degradation and ring opening (Wang, 1990). Some rearranged drimane may form by degradation of angiosperm oleanoids or ring opening of oleananes (Nytoft et al., 2009; Eiserbeck et al., 2011).

Terrigenous crude oils in northwest China are rich in bicyclic alkanes and bicyclic sesquiterpanes. These biomarkers are generally considered to come from higher plants (Fan et al., 1989; Luo et al., 1991).  $C_{14}$ – $C_{16}$ , and  $C_{20}$  bicyclic alkanes and  $C_{15}$ ,  $C_{16}$ , and C<sub>20</sub>-8β(H)-drimane have also been detected in lab-grown Botryococcus braunii. This green alga has been recognised as a major contributor of OM in source rocks, and it can be divided into four chemical races on the basis of their hydrocarbon composition and gene sequences, namely A, B, C and S (Metzger et al., 1985, 1990; Zhang et al., 2007; Volkman, 2014). Complete series of tricyclic terpanes with long side chains have been identified from the chemical race A of B. braunii from the United States and strains of B. braunii from Lake Fuxian in China, although hopanes are rare in B. braunii (Song and Li, 1994). Therefore, B. braunii is also a possible source of these bicyclic biomarkers in sediments. The terpenes that are produced by *B. braunii* may also form bicyclic biomarkers during diagenesis and bacterial degradation in addition to direct synthesis. This information indicates that bicyclic alkanes originate from a variety of sources, such as bacteria and algae and the products of biological degradation. Preliminary studies indicated that the bicyclic sesquiterpane of source rocks and crude oils in the Yanchang Formation may have more chance to come from the abundant B. braunii in the source rocks (Ji et al., 2008, 2010).

Bicyclic sesquiterpanes have been found in a variety of sediments and crude oil, and their geochemical properties have been widely exploited in petroleum exploration. For example, the relative abundances of rearranged drimane and homodrimane are used to investigate the thermal evolution and migration direction of crude oil (Luo et al., 1991; Trindade and Brassell, 1992; Zhang et al., 2004), and the fingerprints of bicyclic sesquiterpanes are applied in oil-source correlation (Al-Arouri et al., 1998; Okunova et al., 2010). However, because the sources of bicyclic biomarkers are complex and their diagenetic evolution is not well understood, the reliability of the applications of bicyclic biomarkers needs to be explored further.

Over the past 10 years, a series of oil reservoirs in lithological traps have been found in the Triassic Yanchang Formation in the Xifeng area, southwest Ordos Basin, northern China. The source of the oil in these reservoirs is the organic-rich Ch 7 section (Ji et al., 2007a; Duan et al., 2008; Yu et al., 2010). The source rocks and crude oil of the Yanchang Formation in the area are rich in bicyclic alkanes, and significant amounts of *B. braunii* have been found in the source rocks. Intervals with high fossil abundance appear to be the main source rock layers in the Ch 7 section (Ji et al., 2010), which indicates that *B. braunii* is not only an important hydrocarbon parent material in the source rocks and crude oil.

In this study, the applications of the geochemical properties of bicyclic alkanes in studies on the depositional environment of source rocks are extended by a detailed analysis and descriptions of the distribution and characteristics of bicyclic alkanes in different environments. Possible changes undergone by bicyclic sesquiterpanes during the migration and accumulation of petroleum and the reliability of their applications in oil-source correlations are evaluated through a comparative study of the source rocks and crude oil.

#### 2. Geological setting

The Ordos Basin is a large Mesozoic depression located in north–central China (Fig. 1). This basin was part of the North China Craton that formed prior to the Paleozoic (Kusky et al., 2007) and became an isolated lake basin in the Middle and Late Triassic. A series of lacustrine and deltaic clastic sediments more than 1000 m thick was deposited in the basin during this time. These sedimentary rocks, which are known as the Yanchang Formation, became the dominant source rocks for Mesozoic oil due to the presence of organic-rich mudstone, carbonaceous shale and oil shale. Sandstone and sand bodies of various sizes tend to form oil reservoirs (Yu et al., 2010; Guo et al., 2012). The Yanchang Formation features 10 oil-bearing beds (from Ch 1 to Ch 10 sections), the lithologies of which are in Table 1. Each oil bed can be further divided into 2 to 3 intervals based on sedimentary cycles and lithologic combinations. Sections Ch 10-Ch 8 are Middle Triassic in age, and sections Ch 7-Ch 1 are considered to be of the Late Triassic based on examinations of sporopollen fossils and determination of zircon U-Pb age (Ji and Meng, 2006; Wang et al., 2014).

The sediments of the Yanchang Formation in the Ordos Basin were clearly controlled by regional tectonic activities. Table 1 shows the complete sedimentary cycle from the beginning of basin development in Ch 10 to the demise of the basin in Ch 1. Three lake transgressions are represented by the Ch 9. Ch 7 and Ch 4 + 5periods. Maximum flooding occurred in Ch 7 and resulted in the source rocks that are widely distributed within the basin (Li et al., 2012). Sandstone layers in different sections of the Yanchang Formation may form Mesozoic petroleum reservoirs in different regions of the basin due to the migration of lake sedimentary center (Yu et al., 2010). An ancient lake can is divided into lakeside, shallow lake, moderately deep lake and deep lake according to water depth, and the moderately deep lake refers to the area between deep lake and shallow lake (Jiang et al., 2007). The main sources of oil in the Xifeng oilfield are the deep and moderately deep lake organic-rich mudstone and oil shale in the Ch 7 section (Ji et al., 2007a). Sandstone in the Ch 8-1 interval beneath Ch 7 forms major petroleum reservoirs in the region. The source rocks are located immediately above the reservoirs (Yang et al., 2004; Guo et al., 2012).

### 3. Material and methods

Oil exploration in the Xifeng area is focused on the Ch 8 to Ch 6 sections of the Yanchang Formation, and wells X30 and X44 are the most complete core drilling in the study area. The majority of samples were collected from the Ch 8 and Ch 7 sections in wells X30 and X44. They not only have higher petroleum potential, also cover various sedimentary environments including lakeside, shallow lake, moderately deep lake and deep lake in the longitudinal based on previous studies (Yang et al., 2004; Ji et al., 2007a; Guo et al., 2012) (Fig. 1). Seventy-two and sixty-two core samples were collected from Ch 8 and Ch 7, respectively. Supplementary samples from the Ch 7-3 interval were collected mainly from wells X40, N4, Zh5, Zh42 and M9 in the adjacent region. The stratigraphic positions of all of the samples were confirmed by correlations between each section. Crude oil samples were collected from eight wells in the Xifeng area. The main reservoir is the Ch 8-1 interval of the Yanchang Formation.

Lipid biomarkers in the samples were extracted using the Soxhlet method. To eliminate potential contaminants, the outer



Fig. 1. Geographic map and sampling well locations in the Xifeng area, Ordos Basin.

surface of each core sample was removed, or fresh grains were selected after a core sample was broken into pieces. The samples were then crushed to fine powder (sub-120 mesh) using a stainless steel mortar and pestle prior to extraction. Between samples, the mortar and pestle were scrubbed with absorbent cotton to remove particulate matter and washed with de-ionised water, methanol and chloroform. Approximately 50–150 g of powder from every sample was weighed, and extracted for 48 h using chloroform prepared in a Soxhlet extractior. The solution was then condensed in a rotary evaporation instrument and desulfurised with activated copper. The extract and crude oil samples were later purified and separated through an alumina-silica gel column and the saturated fraction was extracted by petroleum ether after asphaltenes were precipitated by hexane. All of samples were the drilling core without field exposured for a long time, and the extraction samples were the fresh rocks stripped of core outer in order to reduce and avoid the evaporation of bicyclic alkanes with low carbon number. All reagents used in sample extraction and separation, and other conditions and methods were exactly the same, which made them strictly comparable.

The saturated fractions were analysed using a 6890/5973N gas chromatograph-mass spectrometer (GS-MS) from Agilent Technologies, USA. The GS-MS conditions were as follows: HP-5 capillary column (30 m × 0.25 mm × 0.25 µm); temperature increased from 80 to 290 °C at 4 °C/min and then held for 30 min using high-purity helium as carrier gas; flow rate 1.2 mL min<sup>-1</sup>; linear velocity 40 cm s<sup>-1</sup>; temperature of the ion source 230 °C; quadrupole temperature 150 °C; electron impact energy 70 eV; injection port 280 °C. Biomarkers were identified according to the NIST2002 library. During the analysis, a conventional blank experiment was performed for baseline stabilization and to determine that no

contaminants or residues were present.

The repeated experiments were performed in order to control both pollution and human factors, and the results confirmed the reliability and repeatability of experimental data. Although a part of the  $C_{12}-C_{14}$  bicyclic alkanes has evaporated inevitably during the sampling process, the sample was still able to retain a high abundance of bicyclic alkanes, which indicates the high abundance in the original sample. This abundance differences still exists after the sampling process meets our goal of distinguishing the differences in distribution pattern of bicyclic alkanes.

## 4. Results and discussion

### 4.1. Geochemical characteristics of source rocks

OM in source rocks can be divided into three types based on the kerogen macerals, element ratio and rock pyrolysis (Tissot and Welte, 1984; Peters, 1986). Type I OM contains mainly the hydrogen-rich components derived from phytoplankton, with high oil generation potential. Type III OM consists mainly the hydrogen-poor components derived from higher plants, and generates mainly natural gas. Type II OM is commonly a mixture of the type I and Type III, and can be further divided into partial oil-prone type II<sub>1</sub> and partial gas-prone type II<sub>2</sub>.

Total organic carbon content (TOC), pyrolysis, and chloroform bitumen "A" content of the Ch 8 and Ch 7 sections of the Yanchang Formation in the Xifeng area show that the quality of the source rocks in the different intervals varies significantly (Table 2). TOC of the source rock samples from the Ch 7-3 interval ranged from 0.5 to 40.4 wt.% with an average of 8.1 wt.%; the bitumen "A" content ranged from 398 to 11,881 ppm with an average of 4249 ppm; the

#### Table 1

| Division and sequence of the function in ordos basis |
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| Stratum                          | Stratum                                 |                                      | Thickness(m) Lithology |                            | Lake evolvement         |  |  |
|----------------------------------|---|--------------------------------------|------------------------|----------------------------|-------------------------|--|--|
| Series                           | Form.                                   | Section                              | Oil Layer              |                            |                         |  |  |
| Upper Triassic (T <sub>3</sub> ) | Yanchang Formation (T <sub>2+3</sub> y) | V(T <sub>3</sub> y <sub>5</sub> )    | Ch 1                   |                            | 0–240                   | Black and brown mudstones,<br>light gray siltstones, fine<br>sandstone interlayer with<br>carbonaceous mudstones and<br>coal seams. The interlayer with<br>coal seams, carbonaceous<br>mudstones and tuffs in the<br>bottom. | The disappearance of lake basin,<br>river or flood plain facies  |
|                                  |   | IV (T <sub>3</sub> y <sub>4</sub> )  | Ch 2                   | Ch2-1<br>Ch2-2<br>Ch 2-3   | 40–45<br>40–45<br>45–50 | Gray and dark gray fine<br>sandstone interlayer with<br>brown mudstones. The upper<br>interlayer with carbonaceous<br>mudstones and tuffs.   | The decline of lake basin, river<br>facies in lowstand system tract and<br>shallow - deep lake facies during<br>the flooding                 |
|                                  |   |                                      | Ch 3                   | Ch 3-1                     | 35-50                   | Dark gray mudstones interlayer   |  |
|                                  |   |                                      |                        | Ch 3-2                     | 40-50                   | with brown siltstones and fine   |  |
|                                  |   |                                      |                        | Ch 3-3                     | 45–50                   | sandstone, partially interlayer<br>with coal seams. The upper and<br>lower interlayer with tuffs   |  |
|                                  |   | III (T <sub>3</sub> y <sub>3</sub> ) | Ch 4 + 5               | Ch 4 + 5-1                 | 30–50                   | Black mudstone, carbonaceous<br>mudstones and coal seams<br>interlayer with thin siltstone<br>and fine sandstone,<br>occasionally with tuffs.  | The stabilization of lake basin, river<br>or delta facies in lowstand system<br>tract and moderately deep lake<br>facies during the flooding |
|                                  |   |                                      |                        | Ch 4+5-2                   | 30–50                   | Light gray siltstones and fine<br>sandstone, interlayer with<br>black mudstones.   |  |
|                                  |   |                                      | Ch 6                   | Ch 6-3<br>Ch 6-2           | 35–45<br>35–45          | Light gray and dark gray<br>sandstones interlayer with<br>black mudstones. The layer of<br>bottom interlayer with tuffs.   |  |
|                                  |   |                                      |                        | Ch 6-1                     | 35-40                   | Dark gray mudstones and<br>siltstone interlayer with fine<br>sandstone. The lower interlayer<br>with tuffs.  |  |
|                                  |   |                                      | Ch 7                   | Ch 7-3<br>Ch 7-2<br>Ch 7-1 | 30–40<br>20–50<br>15–55 | Dark gray mudstone,<br>carbonaceous mudstone and oil<br>shale interlayer with thin<br>siltstones. The middle and<br>lower part of interlayer with<br>tuffs.  | The floruit of lake basin, moderately<br>deep - deep lake facies during the<br>flooding  |
| Mid-Triassic (T <sub>2</sub> )   |   | II (T <sub>2</sub> y <sub>2</sub> )  | Ch 8                   | Ch 8-1<br>Ch 8-2           | 35–45<br>40–50          | Gray and light gray arkose<br>quartzites and arkosic arenite<br>interlayer with brown and<br>black mudstones.  | The expansion of lake basin, river-<br>delta facies in highstand system<br>tract   |
|                                  |   | I (T <sub>2</sub> y <sub>1</sub> )   | Ch 9<br>Ch 10          |                            | 90–120<br>150–280       | Gray and dark gray thick arkose<br>quartzite interlayer with dark<br>gray and dark purple<br>mudstones, siltstone and fine<br>sandstone, the interlayer with<br>fine-gravel rocks in the bottom.                             | The beginning of lake basin, river-<br>delta facies in lowstand system<br>tract  |

hydrogen indices (HI) ranged from 85 to 988 mg HC/g TOC with an average of 288 mg HC/g TOC; and the OM was mainly type  $II_1$  and type I based on the van Krevelen diagram (Ji et al., 2007a). The hydrocarbon potential of the Ch 7-3 interval is significantly higher than that of the other intervals. Terrigenous source rocks are the main source of Mesozoic and Cenozoic oil in China, the deep and moderately deep lake sapropelic organic-rich source rocks are considered good source rocks, the TOC, chloroform bitumen "A" content and total hydrocarbon content of which usually greater than 1.0%, 0.12% and 500 ppm, respectively. According to this evaluation criteria defined by Hu et al. (1991), the Ch 7-3 interval is the best source rock in the Yanchang Formation, the Ch 7-2 interval also has higher hydrocarbon potential and belongs to good source rocks. The Ch 7-1 interval has moderate hydrocarbon potential and represents medium quality source rocks. The Ch 8-1 and Ch 8-2 intervals have relatively poor hydrocarbon potential and are mainly non-source rocks. Thermal evolution studies have shown that the vitrinite reflectance (Ro) of the Ch 8 and Ch 7 sections is between 0.69% and 1.0%, which indicates that they have entered the "oil window" and have begun to form significant quantities of petro-leum (Ji et al., 2007b).

The Ch 8 section and Ch 7-1 interval are relatively poor in OM and contain more terrigenous OM than the Ch 7-2 and Ch 7-3 intervals, and the depositional environments of the sediments were deltic and shallow lakes. The Ch 7-2 and Ch 7-3 intervals have abundant oil-prone OM (Table 2). The organic-rich dark mudstone and oil shale were deposited in the reducing environments of deep and moderate-depth lakes and contain significant quantities of sapropelic OM derived from planktonic algae. Some of the source rocks in the Ch 7-3 interval mixed with coarse clastic and terrige-nous OM due to turbidity currents and gravity flows, resulting in mixed types of OM (Ji et al., 2007a; Li et al., 2011).

To fully reflect the distribution of bicyclic alkanes in different stages and sedimentary environments, 27 samples with different

| Table 2  |
|--|
| Geochemical parameters of the source rocks of the Yanchang Formation in the Xifeng area. |

| Stratum | TOC (%)                | $S_1+S_2(mg/g)$          | PI                      | HI (mg/g)         | "A" (ppm)              | HC (ppm)                        | HC/TOC (%)             | OM type               |
|---------|------------------------|--------------------------|-------------------------|-------------------|------------------------|---------------------------------|------------------------|-----------------------|
| Ch 7-1  | 0.33–4.86<br>1.46(25)  | 0.29–16.15<br>4.26(25)   | 0.07 - 0.42<br>0.20(25) | 51–404<br>187(25) | 137–6177<br>1932(4)    | 73.08-3271.68<br>1052.78(4)     | 1.49-10.34<br>5.47(4)  | II <sub>1</sub> , III |
| Ch 7-2  | 0.42–9.51<br>2.46(21)  | 0.33–35.23<br>7.48(21)   | 0.09-0.38<br>0.12(21)   | 52-460<br>229(21) | 161–5509<br>2576(6)    | 78.29–2680.25<br>1517.39(6)     | 0.47-27.07<br>9.71(6)  | I, II <sub>1</sub>    |
| Ch 7-3  | 0.46-40.43<br>8.11(53) | 0.63-167.22<br>31.12(53) | 0.04-0.45<br>0.08(53)   | 85–988<br>288(53) | 398–11,881<br>4249(21) | 326.83-10,648.10<br>2431.78(21) | 0.86-42.76<br>6.59(21) | II <sub>1</sub> , I   |
| Ch 8-1  | 0.29-24.86<br>2.02(64) | 0.10-74.48<br>4.05(64)   | 0.08-0.58<br>0.15 (64)  | 13–341<br>100(64) | 68–14,441<br>2191(11)  | 51.77-6515.26<br>1094.65(11)    | 0.92-4.68<br>2.56(11)  | $II_1, II_2$          |
| Ch 8-2  | 0.41-12.50<br>3.06(17) | 0.24-31.57<br>6.61(17)   | 0.10-0.41<br>0.12(17)   | 29–252<br>110(17) | 364-8502<br>3900(5)    | 157.17–3785.52<br>1698.56(5)    | 1.03-4.08<br>2.67(5)   | 11 <sub>2</sub> , 111 |

Note: minimum - maximum/average(sample number).

generative potentials were selected for biomarker analysis from each interval in the Ch 8 and Ch 7 sections (Table 3). The TOC values for the samples with higher generative potential usually are greater than 1%, and they are mainly distributed in the Ch 7-3 to Ch 7-2 intervals. The OM is generally type I or type II<sub>1</sub>. The carbon isotopic values of the organic carbon are less than -28%.

The productivity index of rock pyrolysis PI is the ratio S<sub>1</sub>/ (S<sub>1</sub> + S<sub>2</sub>). It can be used as a maturity parameter for low mature source rocks, also can indicate the existence of migration oil for mature source rocks. The PI index of vast majority of source rocks (TOC  $\geq$  1%) are less than 0.15, where the PI index of individual sandy source rocks increases slightly, but not exceeds 0.2 (Table 3). The PI index of rich sandy non-source rocks (TOC < 1%) is relatively high, generally from 0.2 to 0.4. According to the criteria of pollutants and foreign oil input by Peters and Cassa (1994): when Tmax at 436–445 °C, PI  $\leq$  0.3; when Tmax at 445–460 °C, PI  $\leq$  0.4. The values of Tmax and PI index for the samples are within a normal range and not showing the ingress of migration oil. Therefore, it is reasonable to use these samples in the studies of molecular organic geochemistry.

#### 4.2. Identification of bicyclic alkanes

Abundant bicyclic alkanes and bicyclic sesquiterpanes were detected in the saturated hydrocarbon fractions of the soluble OM from the Ch 8 and Ch 7 sections of the Yanchang Formation in the Xifeng area. These peaks appear between n-C<sub>12</sub> and n-C<sub>16</sub> after less than 20 min in the total ion current (Fig. 2a). Two groups of bicyclic alkanes, C<sub>12</sub>-C<sub>14</sub> and C<sub>15</sub>-C<sub>16</sub>, appear on the mass fragmentograms at m/z 123 (Fig. 2b). The abundance of the C<sub>15</sub>-C<sub>16</sub> series varies, and the C<sub>12</sub>-C<sub>14</sub> group is generally low or absent, but may be significantly higher in individual samples. The bicyclic alkanes and other terpanes in the source rocks are at least moderately abundant, and the bicyclic alkanes in many samples are more abundant than other terpanes (Fig. 2b).

Structural determination and identification of bicyclic biomarkers were performed based on the literature and mass spectra (Alexander et al., 1984; Noble, 1986; Weston et al., 1989; Peters and Moldowan, 1993). The bicyclic alkanes of the first group are extremely rich in the source rocks and are mainly composed of  $C_{12}$ and  $C_{13}$  compounds. Based on chromatographic and mass spectrometric characteristics, 40 bicyclic alkanes were identified in the source rocks from the Ch 7 section, and the number of  $C_{12}$ ,  $C_{13}$  and  $C_{14}$  compounds are 13, 18 and 9, respectively. Fig. 3 shows a mass

Table 3

Geochemical indicators of samples from the Ch 8-Ch 7 sections of the Yanchang Formation.

| Well | Stratum | Sample No. | Depth (m) | Lithology                   | TOC (%) | Bitumen "A" (ppm) | PI   | HI (mg/g) | Tmax (°C) | $\delta^{13}$ Corg (‰) | Sulphur (%) | OM type |
|------|---------|------------|-----------|-----------------------------|---------|-------------------|------|-----------|-----------|------------------------|-------------|---------|
| X30  | Ch 7-3  | 3-X30      | 1851.6    | Oil shale                   | 24.02   | 7644              | 0.09 | 345       | 442       | -29.8                  | 0.10        |         |
|      |         | 3-3X30     | 1853.1    | Silty mudstone              | 1.01    | 2001              | 0.11 | 152       | 448       | -28.9                  | 0.04        | $II_1$  |
|      |         | 11-X30     | 1859.3    | Oil shale                   | 8.90    | 5984              | 0.08 | 369       | 448       | -32.0                  | 8.10        | 1       |
|      | Ch 8-1  | 7-X30      | 1865.1    | Sandy mudstone              | 0.78    | 230               | 0.33 | 42        | 451       | -26.8                  | 0.02        | 111     |
|      |         | 24-X30     | 1867.8    | Silty mudstone              | 5.79    | 3745              | 0.10 | 233       | 448       | -31.0                  | 0.16        | 1       |
|      |         | 8-X30      | 1877.3    | Silty mudstone              | 0.74    | 221               | 0.31 | 60        | 457       | -26.7                  | 0.02        | 111     |
|      |         | 47-X30     | 1883.6    | Carbonaceous mudstone       | 24.86   | 14,441            | 0.12 | 262       | 447       | -28.7                  | 0.55        | $  _1$  |
|      |         | 49-X30     | 1885.1    | Silty mudstone              | 0.33    | 68                | 0.34 | _         | 454       | -30.8                  | 0.01        | 1       |
|      |         | 51-X30     | 1886.4    | Silty mudstone              | 0.46    | 98                | 0.25 | 43        | 457       | -27.4                  | 0.02        | $II_2$  |
| X44  | Ch 7-1  | 1-X44      | 1969.0    | Siltstone                   | 0.49    | 137               | 0.28 | 57        | 441       | -27.2                  | 0.03        | $II_2$  |
|      | Ch 7-2  | 40-X44     | 1979.3    | Silty mudstone              | 0.99    | 3138              | 0.19 | 350       | 438       | -31.3                  | 0.66        | 1       |
|      | Ch 7-3  | 8-X44      | 2018.0    | Silty mudstone              | 3.97    | 1711              | 0.08 | 371       | 438       | -29.8                  | 1.54        | 1       |
|      |         | 12-X44     | 2020.0    | Oil shale                   | 15.13   | 3379              | 0.06 | 356       | 442       | -30.2                  | 9.76        | 1       |
|      |         | 13-X44     | 2020.5    | Argillaceous fine sandstone | 0.46    | 925               | 0.19 | 178       | 440       | -34.1                  | 1.40        | $  _1$  |
|      |         | 19-X44     | 2023.6    | Silty mudstone              | 0.64    | 535               | 0.19 | 110       | 443       | -28.5                  | 1.41        | $  _1$  |
|      |         | 23-X44     | 2026.0    | Carbonaceous mudstone       | 2.65    | 1076              | 0.06 | 296       | 442       | -32.1                  | 1.16        | 1       |
|      |         | 28-X44     | 2028.4    | Mudstone                    | 0.99    | 398               | 0.21 | 97        | 448       | -29.8                  | 0.04        | $II_2$  |
|      |         | 37-X44     | 2032.6    | Oil shale                   | 40.43   | 7949              | 0.05 | 392       | 449       | -31.2                  | 6.48        | 1       |
|      |         | 40-3X44    | 2034.0    | Oil shale                   | 30.79   | 9356              | 0.04 | 385       | 449       | -29.3                  | 5.85        | 1       |
|      |         | 45-X44     | 2036.9    | Silty mudstone              | 2.49    | 11,881            | 0.19 | 344       | 450       | -33.2                  | 1.12        | 1       |
|      | Ch 8-2  | 46-X44     | 2117.7    | Carbonaceous mudstone       | 9.25    | 8502              | 0.10 | 200       | 443       | -27.4                  | 0.24        | $II_2$  |
| X40  | Ch 7-3  | 84-X40     | 2136.5    | Silty mudstone              | 2.14    | 1844              | 0.15 | 221       | 446       | -27.3                  | 1.05        | $II_2$  |
|      |         | 86-X40     | 2152.0    | Oil shale                   | 10.75   | 3768              | 0.07 | 328       | 449       | -30.7                  | 6.00        | 1       |
| N4   | Ch 7-3  | 36-N4      | 1576.6    | Oil shale                   | 8.63    | 3701              | 0.08 | 283       | 441       | -31.0                  | 7.70        | 1       |
| Zh42 | Ch 7-3  | 88-Zh42    | 2189.2    | Oil shale                   | 8.63    | 2479              | 0.05 | 408       | 450       | -31.6                  | 4.64        | 1       |
| M9   | Ch 7-3  | 94-M9      | 2311.9    | Oil shale                   | 9.39    | 6980              | 0.14 | 272       | 452       | -30.7                  | 1.88        | 1       |
| Zh5  | Ch 7-3  | 102-Zh5    | 1399.0    | Oil shale                   | 23.18   | 7373              | 0.09 | 315       | 442       | -30.6                  | 10.62       | I       |

chromatogram of the  $C_{12}-C_{14}$  bicyclic alkanes from the source rocks in the Ch 7 section of well X44, and Fig. 4 shows the mass spectrometric features of some of the  $C_{12}-C_{14}$  bicyclic alkanes. The order of the position of methyl substitution in naming for the bicyclic alkanes is based on the nomenclature of Alexander et al. (1984).  $C_{12}$ ,  $C_{13}$  and  $C_{14}$  bicyclic alkane, that is dimethyl, trimethyl and tetramethyl decalin, has a molecular weight of 166, 180 and 194 respectively, and has a diagnostic base peak of 95, 165 and 179 in sequence (Fig. 4, Table 4).

The high carbon number bicyclic alkanes in the source rocks are series of  $C_{15}$  and  $C_{16}$  compounds, including drimane and homodrimane, and  $C_{15}$  is generally more abundant. Thirteen compounds were identified based on their retention time and ion chromatography (Table 4, Fig. 5). Fig. 6 shows the mass spectra of several bicyclic alkanes with high carbon numbers.

#### 4.3. Bicyclic alkanes of source rocks

The distributions of the bicyclic alkanes in the source rocks vary greatly and exhibit three patterns. Pattern A primarily contains bicyclic alkanes with lower carbon numbers ( $C_{12}-C_{14}$ ) (Fig. 7). Samples having this pattern are rare in the Ch 7-1 and Ch 8-1

intervals of the Yanchang Formation. They have TOC less than 1 wt.%, contain mainly type III OM and are non-source rocks. Pattern B contains abundant bicyclic C<sub>12</sub>-C<sub>14</sub> alkanes and bicyclic C<sub>15</sub>-C<sub>16</sub> alkanes. Samples having pattern B are present in the Ch 7-3 interval and contained abundant oil-prone OM. Some of these samples could be source rocks, but others are non-source rocks with low TOC (including sandy debris). Pattern C primarily contains bicyclic  $C_{15}-C_{16}$  alkanes with little or no of  $C_{12}-C_{14}$ . Samples having pattern C are the primary organic-rich source rocks in the Ch 7-3 interval, and are also found in the Ch 7-2 and Ch 8-1 intervals, containing oil-prone OM. In order to verify the universality of bicyclic alkane distribution patterns of the Yanchang Formation in the Ordos Basin, the typical source rock samples from the Ch 9 section in Zhidan area, central Ordos Basin and the Ch 7 section in Tongchuan area, southern Ordos Basin had been analysed. The distribution of bicyclic alkanes for samples from both areas showed common Pattern C of excellent source rocks.

Table 5 lists the biomarker parameters of the samples that were studied. The bicyclic alkane-related indicators were calculated based on the m/z 123 mass chromatogram. The relative abundance of bicyclic sesquiterpane is the ratio of the average abundance of the five most abundant bicyclic sesquiterpanes to the abundance of



Fig. 2. Total ion and selected ion chromatograms of the saturated hydrocarbons of the source rocks.



Fig. 3. m/z 123 and 95 + 165 + 179 mass chromatograms of the bicyclic alkanes in the source rocks. The caption of compounds refers to Table 4.

 $C_{30}$  17 $\alpha$ , 21 $\beta$ (H)- hopane (the most abundant hopane). The isomerisation index of drimane is the ratio of the sum of the abundances of two rearranged drimanes (4,4,8,8,9- and 4,4,8,9,9- pentamethyl decalin) to the abundance of drimane. Table 6 lists the biomarkers in Table 5 and the calculation method for each parameter.

Rearranged drimanes are isomers that have rearranged methyl groups resulting from thermal evolution. Two common compounds are 4,4,8,8,9-pentamethyl decalin and 4,4,8,9,9-pentamethyl decalin (Table 4). The isomerisation index of drimane is generally considered to be a sensitive indicator of thermal maturity, and the abundance of rearranged drimanes is proportional to the extent of thermal evolution under certain conditions (Luo et al., 1991; Trindade and Brassell, 1992; Zhang et al., 2004; Gordadzea et al., 2011). The source rocks are mainly in the Ch 7 section of the Yan-chang Formation in the Xifeng area. They experienced similar thermal evolution over geological time, although the burial depth varies with well location. Vitrinite reflectance (Ro) ranged from 0.69% to 0.79% (Ji et al., 2007b). Drimane isomerisation indices for source rocks in the Yanchang Formation vary greatly between 0.94

and 3.0 (Table 5) with no discernible pattern. There is no relationship between the index value and well depth, which indicates that the isomerisation of drimane is not only controlled by thermal effects.

The organic-rich shales with TOC greater than 1.0 wt.% and HI greater than 200 mg HC/g TOC are considered to be the effective source rocks that contributed to the reservoirs in the region (Hu et al., 1991; Ji, 2005). An exponential relationship exists between the isomerisation index of drimane and the TOC of the effective source rocks (Fig. 8). The ratio of rearranged drimane to drimane increased rapidly with decreasing TOC. The abundance of OM is generally believed to be closely related to a reducing sedimentary environment and to reflect high biological productivity and a low deposition rate (Zobaa et al., 2011; Street et al., 2012; Cirilli et al., 2015). This study shows that a reducing environment is conducive not only to the preservation of OM but also may block the rearrangement of drimane in source rocks. Drimane will rearrange more readily in sediments deposited in an oxidizing environment than in sediments deposited in a reducing environment under similar thermal evolution conditions. Rearrangement reaction is



**Fig. 4.** Mass spectra of some of the  $C_{12}$ – $C_{14}$  bicyclic alkanes from the source rocks.

#### Table 4

Identification of bicyclic alkanes and bicyclic sesquiterpenoids.

| Peak no.         | Bicyclic biomarker                   | Formula                         | Molecular weight | Base peak |
|------------------|--------------------------------------|---------------------------------|------------------|-----------|
| 0                | Dimethyl decalin                     | C <sub>12</sub> H <sub>22</sub> | 166              | 95        |
| $\diamond$       | Trimethyl decalin                    | C <sub>13</sub> H <sub>24</sub> | 180              | 165       |
| $\bigtriangleup$ | Tetramethyl decalin                  | C <sub>14</sub> H <sub>26</sub> | 194              | 179       |
| 1                | 4,4,8,8,9-pentamethyl decalin        | C <sub>15</sub> H <sub>28</sub> | 208              | 193       |
| 2                | 4,4,8,9,10-pentamethyl decalin       |                                 |                  |           |
| 3                | 4,4,8,8,10-pentamethyl decalin       |                                 |                  |           |
| 4                | 4,4,8,9,9-pentamethyl decalin        |                                 |                  |           |
| 5                | 8β(H)-drimane                        |                                 |                  | 123       |
| 6,7              | 4,4,9,9,10-pentamethyl decalin       |                                 |                  |           |
| 8                | 4,4,10-trimethyl-9-ethyl-decalin     |                                 |                  |           |
| 9                | 4,4,8,10-tetramethyl-9-ethyl-decalin | C <sub>16</sub> H <sub>30</sub> | 222              | 193       |
| 10               | 4,4,8,9-tetramethyl-8-ethyl decalin  |                                 |                  |           |
| 11               | 8β(H)-homodrimane                    |                                 |                  | 123       |
| 12               | 2,4,4,10-tetramethyl-9-ethyl-decalin |                                 |                  | 193       |
| 13               | 4,4,8,10-tetramethyl-9-ethyl-decalin |                                 |                  |           |

generally considered to be the result of clay and/or acid catalysis during the deposition and diagenesis (Brassell et al., 1984; Farrimond and Telnæs, 1996), and is associated with bacterial activity and thermal effects (Moldowan et al., 1991; Requejo, 1994; Farrimond et al., 1998). The source rocks in the Yanchang Formation experienced a similar thermal evolution. Therefore, there may be more abundant microbial activity in an oxidizing environment.

The homodrimane/drimane ratios of the source rocks in the Yanchang Formation ranged from 0.93 to 3.88 with an average



Fig. 5. m/z 123 and 193 mass chromatograms of C<sub>15</sub>-C<sub>16</sub> bicyclic sesquiterpanes from the source rocks. The caption of compounds refers to Table 4.

value of 1.9 (Table 5), and show a significant abundance of homodrimane. Generally, abundant homodrimane may represent ancient sedimentary environments with high salinity or anoxia (Luo et al., 1991; Al-Arouri et al., 1998). The Ordos Basin was a typical Late Triassic freshwater-brackish water inland lake. The abundance of homodrimane in the source rock may reflect reducing depositional environment of the deep lake.

The drimane/homodrimane ratio was once used as a maturity parameter (Luo et al., 1991). The ratio gradually increases with Ro up to 1.3% and decreases with Ro above 1.3%. The Ch 8 and Ch 7 sections of the Yanchang Formation in the Xifeng area have a same thermal history and similar thermal maturities, and their Ro values are less than 1.0% (Ji et al., 2007b). Therefore, the difference in the homodrimane/drimane ratios of the different intervals and the different samples may primarily reflect differences in sedimentary microfacies and organic constituents. Samples with high homodrimane/drimane ratios generally have heavier organic carbon isotope values, which indicate that the samples contain more OM derived from terrigenous higher plants (Noble et al., 1986). Also, the data of source rocks of the Yanchang Formation in the study area roughly shows this trend (Fig. 9). Abundant bicyclic alkanes were detected in the Tertiary lacustrine source rocks and coal in the Qaidam Basin and demonstrate that the relative abundance of  $8\beta(H)$ -homodrimane is greater than that of  $8\beta(H)$ -drimane; the alkanes are considered to contain abundant higher plant OM (Luo et al., 1991). The source rocks of the Yanchang Formation in the Ordos Basin are comparable to the Tertiary source rocks in Qaidam Basin due to their similar inland lake environments and biological origin of OM. Both of them have an obvious high abundance of homodrimane (Table 5), reflecting abundant terrigenous OM input.

In addition, the drimane isomerisation index of the source rocks in the study area is positively correlated with the hopane parameter Tm/Ts (Fig. 10). A decrease in the Tm/Ts ratio generally reflects an increase in the thermal maturity of a sedimentary environment and may also reflect different sources of parent material under similar thermal evolution conditions (Seifert and Moldowan, 1978; Moldowan et al., 1986). The Tm/Ts ratios of the source rocks in the Yanchang Formation in the Xifeng area range from 0.25 to 4.63, and there is no correlation between the ratio and drilling depth. Such a wide range of Tm/Ts ratios may reflect significant differences in the OM composition of the source rocks and input of terrigenous OM into the lake. Sandy gravel and silty interbeds and clumps are widely distributed in the argillaceous source rocks of the Yanchang Formation. Turbidity currents and gravity flows are the likely carriers of terrigenous OM into deep-water environments (Li et al., 2011).

#### 4.4. Bicyclic alkanes of crude oil

Crude oils from different wells in the study area also contain abundant bicyclic alkanes. Their distribution is extremely consistent, and shows the same pattern as pattern C in the source rock extracts; that is,  $C_{15}-C_{16}$  are the dominant bicyclic alkanes, and individual C<sub>14</sub> only appears in low abundance (Table 5, Fig. 7). The abundance parameters  $\Sigma(C_{15}-C_{16})/5C_{30}\alpha\beta$  of the bicyclic sesquiterpane of the crude oil range between 0.85 and 1.28 with individual values of up to 1.75 and an average of 1.2. The isomerisation parameters of drimane range between 0.88 and 1.10 with an average of 1.0. The homodrimane/drimane ratios range between 0.73 and 0.93 with an average of 0.8. Although the crude oil and source rocks contain bicyclic alkanes with the same carbon numbers, their relative abundance and parameter values differ (Table 5; Fig. 7).  $8\beta(H)$ -drimane is the main peak of the bicyclic alkanes in the crude oil,  $8\beta(H)$ -homodrimane is the second largest peak, and rearranged drimane has lower abundance. Most of the source rocks in the Ch 7 section have a main peak of  $8\beta(H)$ homodrimane or rearranged drimane, and  $8\beta(H)$ -drimane is the second peak. This difference may be caused by two factors: the



Fig. 6. Mass spectra of several C<sub>15</sub>-C<sub>16</sub> bicyclic sesquiterpanes from the source rocks.

crude oil may be mixed with hydrocarbons from source rocks outside the Yanchang Formation, or the bicyclic sesquiterpanes may have undergone significant changes during migration and accumulation. The highest abundance of bicyclic sesquiterpane occurs in the sediments of freshwater lakes and swamps (Fan et al., 1989). The relative abundance decreases during the evolution from freshwater to brackish and salt environments, and crude oil derived from saltwater sediments has a greater relative abundance of  $C_{12}-C_{14}$  bicyclic alkanes than that from brackish and freshwater sediments. The high abundance of  $C_{15}-C_{16}$  bicyclic alkanes that was

detected in the source rocks and crude oil of the Yanchang Formation in the Xifeng area indicates a freshwater lake environment (Figs. 5 and 7; Table 5).

Gammacerane is a pentacyclic triterpenoids biomarker, and earlier studies had thought it derives from the protozoan Tetrahymena (Ourisson et al., 1987; ten Haven et al., 1989; Venkatesan, 1989). Later, researchers found the source of tetrahymenol, the precursor of gammacerane, consists of bacteria on which Tetrahymena feeds (Sinninghe Damsté et al., 1995). The relative abundance of gammacerane to  $C_{30}\alpha\beta$ -hopane is called the gammacerane index



Fig. 7. Distribution pattern of bicyclic alkanes and bicyclic sesquiterpanes of the source rocks.

#### Table 5

Geochemical parameters of the alkane hydrocarbon of source rocks and crude oil in the Yanchang Formation.

| Sample    | Well   | Stratum | Sample   | Depth  | Pr/Ph | Pr/nC <sub>17</sub> | Ph/nC <sub>18</sub> | Bicyclic alkanes                            |                        |                         |         | Tri-terpene | Hopan | e   |   |
|-----------|--------|---------|----------|--------|-------|---------------------|---------------------|---|------------------------|-------------------------|---------|-------------|-------|---|---|
| type      |        |         | no.      | (m)    |       |                     |                     | $\sum (C_{15} - C_{16})/5C_{30}\alpha\beta$ | Re-drimane/<br>Drimane | Homodrimane/<br>Drimane | Pattern | /Hopane     | Tm/Ts | $\frac{\Sigma(C_{27}+C_{29})}{\Sigma C_{31^+}}$ | <u>Gammacerane</u><br>0.5C <sub>31</sub> αβ |
| Source    | X30    | Ch 7-3  | 3-X30    | 1851.6 | 1.44  | 0.15                | 0.11                | 7.07  | 1.48                   | 0.93                    | С       | 0.13        | 1.39  | 2.37  | 0.31  |
| rock      |        |         | 3-3X30   | 1853.1 | 1.42  | 0.38                | 0.28                | 1.69  | 2.40                   | 0.93                    | С       | 0.16        | 1.90  | 1.67  | 0.19  |
|           |        |         | 11-X30   | 1859.3 | 1.85  | 0.28                | 0.17                | 2.93  | 2.11                   | 1.00                    | С       | 0.16        | 2.47  | 1.79  | 0.29  |
|           |        | Ch 8-1  | 7-X30    | 1865.1 | 1.55  | 0.48                | 0.29                | 3.00  | 2.09                   | 1.64                    | А       | 0.31        | 1.03  | 0.86  | 0.18  |
|           |        |         | 24-X30   | 1867.8 | 3.93  | 1.64                | 0.29                | 4.00  | 2.82                   | 2.36                    | В       | 0.11        | 2.94  | 2.03  | 0.23  |
|           |        |         | 8-X30    | 1877.3 | 1.96  | 0.81                | 0.35                | 3.00  | 1.89                   | 1.89                    | Α       | 0.40        | 0.72  | 0.94  | 0.59  |
|           |        |         | 47-X30   | 1883.6 | 4.04  | 1.08                | 0.29                | 2.26  | 1.48                   | 2.95                    | В       | 0.08        | 0.28  | 1.10  | 0.22  |
|           |        |         | 49-X30   | 1885.1 | 0.95  | 0.57                | 0.63                | 0.18  | 1.67                   | 3.00                    | С       | 0.50        | 0.37  | 1.36  | 0.36  |
|           |        |         | 51-X30   | 1886.4 | 1.23  | 0.58                | 0.47                | 0.17  | 1.50                   | 3.17                    | С       | 0.27        | 2.56  | 2.04  | 0.28  |
|           | X44    | Ch 7-1  | 1-X44    | 1969.0 | 1.41  | 0.52                | 0.34                | 0.26  | 1.50                   | 3.44                    | А       | 0.14        | 5.10  | 0.95  | 0.57  |
|           |        | Ch 7-2  | 40-X44   | 1979.3 | 1.14  | 0.52                | 0.43                | 1.64  | 3.00                   | 1.92                    | С       | 0.06        | 4.63  | 1.20  | 0.35  |
|           |        | Ch 7-3  | 8-X44    | 2018.0 | 1.47  | 0.21                | 0.15                | 0.87  | 1.56                   | 1.58                    | В       | 0.08        | 0.95  | 1.46  | 0.21  |
|           |        |         | 12-X44   | 2020.0 | 1.40  | 0.18                | 0.12                | 2.44  | 1.26                   | 1.63                    | С       | 0.15        | 1.00  | 1.95  | 0.23  |
|           |        |         | 13-X44   | 2020.5 | 1.42  | 0.30                | 0.19                | 0.82  | 1.86                   | 1.52                    | В       | 0.12        | 0.78  | 1.02  | 0.20  |
|           |        |         | 19-X44   | 2023.6 | 1.33  | 0.42                | 0.29                | 2.17  | 2.13                   | 1.75                    | В       | 0.10        | 0.27  | 1.20  | 0.29  |
|           |        |         | 23-X44   | 2026.0 | 1.59  | 0.29                | 0.19                | 0.98  | 2.10                   | 1.58                    | В       | 0.08        | 2.50  | 1.23  | 0.16  |
|           |        |         | 28-X44   | 2028.4 | 1.61  | 0.50                | 0.26                | 1.40  | 2.54                   | 1.43                    | В       | 0.11        | 0.25  | 0.88  | 0.17  |
|           |        |         | 37-X44   | 2032.6 | 1.76  | 0.18                | 0.12                | 8.00  | 1.50                   | 1.33                    | С       | 0.34        | 0.88  | 3.00  | 0.20  |
|           |        |         | 40-3X44  | 2034.0 | 1.56  | 0.28                | 0.16                | 0.05  | 1.33                   | 2.80                    | С       | 0.16        | 0.90  | 2.75  | 0.19  |
|           |        |         | 45-X44   | 2036.9 | 1.64  | 0.38                | 0.21                | 0.70  | 1.63                   | 1.46                    | С       | 0.07        | 1.58  | 1.30  | 0.21  |
|           |        | Ch 8-2  | 46-X44   | 2117.7 | 4.15  | 1.89                | 0.36                | 2.60  | 1.81                   | 3.88                    | В       | 0.16        | 0.90  | 2.56  | 0.19  |
|           | X40    | Ch 7-3  | 84-X40   | 2136.5 | 1.49  | 0.27                | 0.18                | 2.60  | 2.43                   | 1.14                    | В       | 0.16        | 4.00  | 1.62  | 0.29  |
|           |        |         | 86-X40   | 2152.0 | 1.67  | 0.22                | 0.13                | 1.60  | 1.61                   | 2.00                    | С       | 0.24        | 2.63  | 2.48  | 0.19  |
|           | N4     | Ch 7-3  | 36-N4    | 1576.6 | 1.46  | 0.33                | 0.23                | 0.83  | 1.80                   | 1.47                    | С       | 0.05        | 1.92  | 1.38  | 0.17  |
|           | Zh42   | Ch 7-3  | 88-Zh42  | 2189.2 | 1.79  | 0.25                | 0.12                | 1.31  | 1.81                   | 2.48                    | С       | 0.13        | 3.13  | 1.89  | 0.17  |
|           | M9     | Ch 7-3  | 94-M9    | 2311.9 | 0.97  | 0.35                | 0.40                | 3.48  | 2.60                   | 1.20                    | С       | 0.10        | 3.92  | 2.04  | 0.21  |
|           | Zh5    | Ch 7-3  | 102-Zh5  | 1399.0 | 1.00  | 0.17                | 0.18                | 0.59  | 0.94                   | 1.19                    | С       | 0.10        | 0.71  | 2.17  | 0.30  |
| Crude oil | X29-23 | Ch 8-1  | Y-X29-23 | _      | 1.25  | 0.51                | 0.39                | 1.75  | 1.03                   | 0.73                    | С       | 0.12        | 0.98  | 1.93  | 0.32  |
|           | X28-16 | Ch 8-1  | Y-X28-16 | _      | 1.22  | 0.58                | 0.43                | 1.13  | 0.97                   | 0.80                    | С       | 0.09        | 0.07  | 1.80  | 0.35  |
|           | X36-24 | Ch 8-1  | Y-X36-24 | _      | 1.19  | 0.47                | 0.37                | 1.63  | 1.00                   | 0.73                    | С       | 0.11        | 1.00  | 1.72  | 0.27  |
|           | X167   | Ch 8-1  | Y-X167   | -      | 1.23  | 0.58                | 0.45                | 1.05  | 0.88                   | 0.82                    | С       | 0.08        | 0.88  | 1.66  | 0.25  |
|           | X181   | Ch 8-1  | Y-X181   | -      | 1.21  | 0.62                | 0.48                | 0.90  | 1.02                   | 0.83                    | С       | 0.08        | 0.80  | 1.60  | 0.25  |
|           | X163   | Ch 8-1  | Y-X163   | _      | 1.36  | 0.41                | 0.28                | 1.28  | 1.10                   | 0.80                    | С       | 0.09        | 1.03  | 1.53  | 0.36  |
|           | D75-68 | Ch 8    | Y-D75-68 | _      | 1.33  | 0.53                | 0.38                | 0.85  | 0.91                   | 0.82                    | С       | 0.07        | 0.86  | 1.55  | 0.28  |
|           | X130   | Ch 8    | Y-X130   | -      | 1.26  | 0.57                | 0.46                | 1.05  | 1.10                   | 0.93                    | С       | 0.07        | 0.96  | 1.70  | 0.24  |

#### Table 6

Explanation of the related biomarker parameters.

| Biomarker Parameter                             | Abundance ratio   |
|---|---|
| Pr/Ph   | Pristane to phytane   |
| Pr/nC17; Ph /nC18                               | Pristane to $nC_{17}$ ; Phytane to $nC_{18}$  |
| $\sum (C_{15} - C_{16}) / 5C_{30} \alpha \beta$ | The average of five highest bicyclic sesquiterpenes to $C_{30}\alpha\beta$ -hopane                          |
| Re-drimane/Drimane                              | Rearranged drimane to drimane   |
| Tri-terpene/Hopane                              | Tricyclic terpene to $C_{30}\alpha\beta$ -hopane  |
| Tm/Ts   | 17α(H)-trinorhopane to 18α(H)-trinorhopane  |
| $\sum (C_{27} + C_{29}) / \sum C_{31} +$        | $\sum C_{27}$ -trinorhopane and $\sum C_{29}$ -norhopane to $\sum C_{31}$ - $C_{35}\alpha\beta$ -homohopane |
| Gammacerane/ $0.5C_{31}\alpha\beta$             | Gammacerane to 0.5 $\times$ $C_{31}\alpha\beta$ -homohopane 22(S $+$ R)                                     |

(GI), and is a common indicator of the salinity of ancient sedimentary environments. Studies have shown that the abundance of gammacerane increases with increasing water salinity, and high GI is an indication of highly saline reducing depositional environments and stratification of the water column (Moldowan et al., 1985; Peters and Moldowan, 1993; Schoell et al., 1994; Sinninghe Damsté et al., 1995; Zhu et al., 2005). The source rocks and crude oil in the Yanchang Formation in the Xifeng area have GIs generally less than 0.1, indicating typical freshwater sedimentary features. In order to better reflect slight changes in salinity, the ratio of gammacerane abundance to the average abundance of  $C_{31}$ –22S and  $C_{31}$ –22R hopanes was selected to supplement GI. The GI in most source rocks of the Ch 7 and Ch 8 sections is in the range from 0.16 to 0.30, with a small number of samples as high as 0.5 or more (Table 5). These data indicate that freshwater environments prevailed in the Ordos Basin during the deposition of the Ch 7 and Ch 8 sections, but with interludes of brackish water for short periods. Two ecological types of *B. braunii* were found in the Ch 7 and Ch 8 sections in the Xifeng area, suggesting that the lake water probably had a slight pulse of salinity at that time (Ji et al., 2010).

### 4.5. Reliability of bicyclic alkane in oil-source correlations

The source of petroleum in the Yanchang Formation in the Xifeng area is inferred to be the Ch 7 section of the Yanchang Formation, particularly the black mudstone, carbonaceous shale and



Fig. 8. Relationship between the drimane isomerisation index and TOC.



Fig. 9. Relationship between the homodrimane/drimane ratio and organic carbon isotope value in well X44.



Fig. 10. Relationship between the drimane isomerisation index and Tm/Ts ratio.

oil shale in the Ch 7-3 interval (Ji et al., 2007a; Duan et al., 2008). The results of oil-source correlations using conventional biomarker parameters are consistent with this reasoning (Ji, 2005). Several

hopane parameters for the effective source rocks and crude oil from this study are comparable, which also indicates that the Ch 7-3 interval is the main source for oil in the reservoir of the Ch 8 section in the study area. Table 5 list the hopane parameters Tm/Ts,  $\Sigma(C_{27} + C_{29})/\Sigma C_{31+}$  and gammacerane/0.5 $C_{31}\alpha\beta$  of the source rocks and crude oil; they often were used separately as the indicator of thermal maturity, parent material of OM and salinity of water medium; the averages in the source rocks are 1.84, 1.68 and 0.26, respectively, and the averages in the crude oil are 1.03, 1.69 and 0.29, respectively. The lithologic trap reservoirs with ultra-low porosity and permeability in the Ch 8-1 interval clung the source rocks in the Ch 7-3 interval, and the crude oil is found to be shortdistance migrated and good confinement (Ji, 2005; Yao et al., 2013). Therefore, the similar distributions and averages of the parameters also indicate an oil-source relationship.

However, the peak shapes and relative abundances of the bicyclic sesquiterpanes in the crude oil and source rocks are significantly different. The parameter values are also significantly different (Table 5), and the bicyclic sesquiterpanes show greater variability than the other terpanes, especially the hopanes. The abundance parameters for the bicyclic alkane in the source rocks in the Yanchang Formation range between 0.59 and 7.07 with an average of 2.4. The isomerisation parameters of drimane range between 0.94 and 3.0 with an average of 1.9. The homodrimane/ drimane ratios range between 0.93 and 3.88 with an average of 1.8. These values for the source rocks are greater than those of the crude oil: their averages are approximately twice the average corresponding values of the bicyclic alkanes in the crude oil. The significant differences among the bicyclic alkanes for the source rocks and the crude oil indicate that oil-source correlations that are based on the relative abundance of bicyclic sesquiterpanes and related geochemical parameters are not reliable. However, the fingerprint characteristics of bicyclic sesquiterpanes have often been used in oil-source correlations and comparisons of crude oil in previous studies (Al-Arouri et al., 1998; Okunova et al., 2010).

The abundance of bicyclic sesquiterpanes of the crude oil is much lower than that of the source rocks (Table 5), which indicates that the bicyclic sesquiterpanes suffered more serious degradation than the hopanes during the discharge of hydrocarbons from the source rocks and migration into the reservoir. Perhaps the relative oxidised reservoir environment in the Ch 8 section is not conducive to the preservation of bicyclic sesquiterpanes due to microbial activity. Previous studies have found that bicyclic sesquiterpanes were completely degraded by bacterial action before the beginning of biodegradation of steranes and hopanes (Alexander et al., 1983), which indicates that weak microbial activities may have a greater effect on bicyclic sesquiterpanes, although sufficient evidences indicate that the crude oil of the Yanchang Formation did not experience distinct biodegradation.

The average of the isomerisation parameters of the rearranged drimane of the crude oil is also much less than that of the main source rocks. This result indicates that the rearranged drimane may suffer more severe degradation than the drimane during petroleum migration and accumulation for a consistent parent material and under similar thermal maturity and perhaps in the presence of selective degradation. The average homodrimane/drimane ratio of the source rocks is significantly greater than that of the crude oil. These data indicate that homodrimane experiences a greater loss than drimane during petroleum migration or after entering the reservoir. This loss may be caused by selective microbial degradation (Williams et al., 1986) and possibly water washing (Kuo, 1994).

The distribution of  $Pr/nC_{17}$  and  $Ph/nC_{18}$  ratio of source rocks in the Yanchang Formation has a wide range, from 0.15 to 1.89 with an average of 0.49 and from 0.11 to 1.63 with an average of 0.26, respectively (Table 5). The ratios of most of organic-rich source

rocks are less than 0.40 and 0.30 respectively. The parameter values of crude oil are greater than 0.40 and 0.30, distributed from 0.41 to 0.62 with an average of 0.53 and from 0.37 to 0.48 with an average of 0.41 respectively, which are generally higher than that of source rocks. N-alkanes are easier to be degraded than isoprenoid due to selective microbial degradation, thus  $Pr/nC_{17}$  and  $Ph/nC_{18}$  ratio of crude oil will increase when it is biodegraded. However, the source rocks and crude oil in the Yanchang Formation have a similar level of thermal evolution, the increase of  $Pr/nC_{17}$  and  $Ph/nC_{18}$  ratio of crude oil indicates that slight biodegradation might occur for crude oil. A few of core samples (24-X30, 47-X30 and 46-X44) with  $Pr/nC_{17}$  ratio of 1.0 or more may be related to the component of organic matter, also there might be an intensive biodegradation.

The study showed that the crude oil in the Xifeng area was derived mainly from source rocks with pattern C for bicyclic alkanes in the Ch 7-3 interval; the organic-rich sediments with pattern B for bicyclic alkanes in other sections also contributed to the formation of the oil. The oil in the Yanchang Formation in the area mainly stored in the Ch 8-1 interval, which is near the upper Ch 7-3 interval and has similar characteristics, and the source rocks of the Ch 7-3 interval have a high petroleum potential.

### 5. Conclusions

Geochemical analyses of the source rocks from the Yanchang Formation in the Xifeng area indicate that dark mudstone and oil shale in the Ch 7-3 interval was deposited in a reducing environment in deep and moderately deep lakes, mainly contains type  $II_1$  and type I OM, and is the main source of hydrocarbons in the area. The Ch 7-1 and Ch 7-2 intervals also contributed to the oil. Source rocks of the Ch 7 section in different wells and at different depths have similar thermal histories (Ro from 0.69% to 0.79%), and have begun to generate petroleum.

Two groups of abundant bicyclic alkanes,  $C_{12}-C_{14}$  and  $C_{15}-C_{16}$ , were detected in the Ch 7 and Ch 8 sections of the Yanchang Formation. The main bicyclic alkanes in the first group are  $C_{12}$  and  $C_{13}$ , and the second group generally contains more abundant  $C_{15}$  bicyclic alkanes. The distributions of bicyclic alkanes in the source rocks have three patterns: A) mainly bicyclic alkanes with lower carbon numbers, which are present in the non-source rocks of the Ch 8-1 and Ch 7-1 intervals; B) two groups of bicyclic alkanes of equivalent abundance, which are common in the source rocks of interval Ch 7-3 and are also found in sandy non-source rocks; and C) mainly bicyclic alkanes with high carbon numbers, which are predominantly found in the source rocks of interval Ch 7-3 and also in sediments that contain oil-prone type of OM in intervals Ch 8-1 and Ch 7-2.

Although the source rocks in the Ch 7 section have similar thermal histories, the differences in the abundance ratios of rearranged drimane and drimane are significant, which indicates that drimane rearrangement is not only controlled by thermal evolution but may also be related to depositional environment. Strong reducing conditions may suppress the rearrangement of drimane in source rocks. The carbon isotope values of OM of the samples with higher abundance ratios of homodrimane and drimane are generally heavier, which indicates that they comprise mainly terrigenous OM from higher plants. The drimane isomerisation parameter of the source rocks and the hopane parameter Tm/Ts are positively correlated. The differences in the Tm/Ts ratio are significant and do not vary regularly with depth, and may be related to changes in the OM composition of the source rocks. Turbidity currents and gravity flows caused the frequent input of large amounts of terrigenous OM into the deepwater source rocks.

All of the crude oil samples in the Xifeng area are rich in bicyclic alkanes. Their features are similar and show abundant  $C_{15}$ – $C_{16}$ 

bicyclic alkanes. The features also indicate that the crude oil mainly came from the source rocks of the Ch 7-3 interval, which has pattern C of bicyclic alkanes. The relative abundance of the bicyclic alkanes in the crude oil and source rocks clearly differ, although they have the same high carbon number. All of the crude oil samples have an  $8\beta(H)$ -drimane main peak, and the abundance of rearranged drimane is low. Most of the source rocks have main peaks that correspond to  $8\beta(H)$ -homodrimane or rearranged drimane. The distributions of bicyclic alkanes show significant differences between the crude oil and source rock samples. Weak microbial action, selective degradation and water washing during migration and accumulation of hydrocarbons were likely important factors. These results indicate that oil-source correlations that are based on the relative abundance of bicyclic alkanes and their related geochemical parameters may be unreliable even though the bicyclic alkanes in the crude oil and source rocks have similar origins.

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#### References

- Alexander, R., Kagi, R.I., Noble, R., Volkman, J.K., 1984. Identification of some bicyclic alkanes in petroleum. Org. Geochem. 6, 63–72.
- Alexander, R., Kagi, R.I., Woodhouse, G.W., Volkman, J.K., 1983. The geochemistry of some biodegraded Australian oils. Aust. Petrol. Explor. Assoc. J. 23, 53–63.
- Al-Arouri, K.R., McKirdy, D.M., Boreham, C.J., 1998. Oil-source correlation as a tool in identifying the petroleum systems of the southern Taroom Trough, Australia. Org. Geochem. 29, 713–734.
- Brassell, S.C., McEvoy, J., Hoffmann, C.F., Lamb, N.A., Peakman, T.M., Maxwell, J.R., 1984. Isomerisation, rearrangement and aromatisation of steroids in distinguishing early stages of diagenesis. Org. Geochem. 6, 11–23.
- Cirilli, S., Buratti, N., Gugliotti, L., Frixa, A., 2015. Palynostratigraphy and palynofacies of the Upper Triassic Streppenosa Formation (SE Sicily, Italy) and inference on the main controlling factors in the organic rich shale deposition. Rev. Palaeobot. Palvnol. 218, 67–79.
- Duan, Y., Wang, C.Y., Zheng, C.Y., Wu, B.X., Zheng, G.D., 2008. Geochemical study of crude oils from the Xifeng oilfield of the Ordos basin, China. J. Asian Earth Sci. 31, 341–356.
- Eiserbeck, C., Nelson, R.K., Grice, K., Curiale, J., Reddy, C.M., Raiteri, P., 2011. Separation of 18α(H)-, 18β(H)-oleanane and lupane by comprehensive twodimensional gas chromatography. J. Chromatogr. A 1218, 5549–5553.
- Fan, P., Philp, R.P., Meng, Q., Cheng, X., Li, J., Yu, X., Li, Z., Chen, N., 1989. Biomarkers indicating sedimentary paleoenvironments. Sci. China B 32 (2), 242–256.
- Farrimond, P., Taylor, A., Telnæs, N., 1998. Biomarker maturity parameters: the role of generation and thermal degradation. Org. Geochem. 29 (5–7), 1181–1197.
- Farrimond, P., Telnæs, N., 1996. Three series of rearranged hopanes in Toarcian sediments (northern Italy). Org. Geochem. 25 (3/4), 165–177.
- Gordadzea, G.N., Okunova, T.V., Giruts, M.V., Erdnieva, O.G., Koshelev, V.N., 2011. Petroleum C<sub>15</sub> polyalkyl substituted bicyclo[4.4.0] decanes (sesquiterpanes) as oil maturity indicators (illustrated by the example of Jurassic and Cretaceous oils of Kalmykia). Petrol. Chem. 51 (2), 117–122.
- Guo, Y., Liu, J., Yang, H., Liu, Z., Fu, J., Yao, J., Xu, W., Zhang, Y., 2012. Hydrocarbon accumulation mechanism of low permeable tight lithologic oil fields in the Yanchang Formation, Ordos basin, China. Petrol. Explor. Dev. 39 (4), 447–456.
- Hu, J.Y., Huang, D.F., Xu, S.B., Gan, K.W., Xue, S.H., Ying, F.X., 1991. The Basis of Nonmarine Petroleum Geology in China. Petroleum Industry Press, Beijing, China, pp. 164–234 (in Chinese).
- Ji, L., 2005. The Oi1-source Correlation, Biological Source and Paleo-climate Studies of Triassic Source Rocks in Xifeng Area of East Gansu Province (PhD thesis). Faculty of Earth Sciences, China University of Geosciences, Wuhan, China, pp. 1–188 (in Chinese with English abstract).
- Ji, L., Li, L., Wu, T., 2007b. Thermal evolution of source rocks in Yanchang Formation, Xifeng Area, East Gansu Province. J. Southwest Petrol. Univ. 29 (3), 28–31 (in Chinese with English abstract).
- Ji, L., Meng, F., 2006. Palynology of Yanchang Formation of Middle and Late Triassic

in eastern Gansu and its paleoclimatic significance. J. China Univ. Geosci. 17 (3), 209–220.

- Ji, L., Song, Z., Li, J., 2008. Characteristic of biomarkers originating from *Botryococcus* in the Triassic Lacustrine hydrocarbon source rocks and crude oils in the Ordos Basin. Acta Micropalaeontol. Sin. 25 (3), 281–290 (in Chinese with English abstract).
- Ji, L., Wu, T., Li, L., 2007a. Geochemical characteristic of the kerogen in source rocks from the Yanchang Formation in Xifeng area, east Gansu Province. Petrol. Explor. Develop. 34 (4), 424–428 (in Chinese with English abstract).
- Ji, L., Yan, K., Meng, F., Zhao, M., 2010. The oleaginous *Botryococcus* from the Triassic Yanchang Formation in Ordos basin, Northwestern China: morphology and its paleoenvironmental significance. J. Asian Earth Sci. 38 (1), 175–185.
- Jiang, Z., Chen, D., Qiu, L., Liang, H., Ma, J., 2007. Source-controlled carbonates in a small Eocene half-graben lake basin (Shulu Sag) in central Hebei Province, North China. Sedimentology 54 (2), 265–292.
- Kuo, L.C., 1994. An experimental-study of crude-oil alteration in reservoir rocks by water washing. Org. Geochem. 21, 465–479.
- Kusky, T., Li, J., Santosh, M., 2007. The Paleoproterozoic North Hebei orogen: North China craton's collisional suture with the Columbia supercontinent. Gondwana Res. 12, 4–28.
- Li, X., Chen, Q., Liu, H., Wan, Y., Wei, L., Liao, J., Long, L., 2011. Features of sandy debris flows of the Yanchang Formation in the Ordos basin and its oil and gas exploration significance. Acta Geol. Sin. 85 (5), 1187–1202.
- Li, X., Liu, X., Zhou, S., Liu, H., Chen, Q., Wang, J., Liao, J., Huang, J., 2012. Hydrocarbon origin and reservoir forming model of the Lower Yanchang Formation, Ordos Basin. Petrol. Explor. Dev. 39 (2), 184–193.
- Luo, B., Wang, Y., Meng, Q., Yang, X., Li, X., Chen, N., 1991. Geochemistry of bicyclic alkanes in sediments, coal and crude oil. Sci. China B 34 (3), 363–376.
- Metzger, P., Berkaloff, C., Casadevall, E., Couté, A., 1985. Alkadiene- and botryococcene- producing races of wild strains of *Botryococcus braunii*. Phytochemistry 24 (10), 2305–2312.
- Metzger, P., Allard, B., Casadevall, E., Berkaloff, C., Couté, A., 1990. Structure and chemistry of a new chemical race of *Botryococcus braunii* (Chlorophyceae) that produces lycopadiene, a tetraterpenoid hydrocarbon. J. Phycol. 26, 258–266.
- Moldowan, J.M., Fago, F.J., Carlson, R.M.K., Young, D.C., van Duyne, G., Clardy, J., Schoell, M., Pillinger, C.T., Watt, D.S., 1991. Rearranged hopanes in sediments and petroleum. Geochim. Cosmochim. Acta 55, 3333–3353.
- Moldowan, J.M., Seifert, W.K., Gallegos, E.J., 1985. Relationship between petroleum composition and depositional environment of petroleum source rocks. AAPG Bull. 69, 1255–1268.
- Moldowan, J.M., Sundararaman, P., Schoell, M., 1986. Sensitivity of biomarker properties to depositional environment and/or source input in the Lower Toarcian of SW-Germany. Org. Geochem. 10, 915–926.
- Noble, R.A., 1986. A Geochemical Study of Bicyclic Alkanes and Diterpenoid Hydrocarbons in Crude Oils, Sediments and Coals (PhD thesis). Department of Organic Chemistry, University of Western Australia, Crawley, Australia, pp. 1–365.
- Noble, R.A., Alexander, R., Kagi, R.I., Knox, J., 1986. Identification of some diterpenoid hydrocarbons in petroleum. Org. Chem. 10, 825–829.
- Nytoft, H.P., Samuel, O.J., Kildahl-Andersen, G., Johansen, J.E., Jones, M., 2009. Novel C<sub>15</sub> sesquiterpanes in Niger Delta oils: structural identification and potential application as new markers of angiosperm input in light oils. Org. Geochem. 40, 595–603.
- Okunova, T.V., Badmaev, C.M., Giruts, M.V., Erdnieva, O.G., Koshelev, V.N., Gordadze, G.N., 2010. Characteristics of the distribution of bi-, tri-, tetra-, and pentacyclic terpanes in Kalmykia crude oils. Chem. Tech. Fuels Oils 46, 119–126.
- Ourisson, G., Rohmer, M., Poralla, K., 1987. Prokaryotic hopanoids and other polyterpenoid sterol surrogates. Annu. Rev. Microbiol. 41, 301–333.
- Peters, K.E., 1986. Guidelines for evaluating petroleum source rock using programmed pyrolysis. AAPG Bull. 70, 318–329.
- Peters, K.E., Cassa, M.R., 1994. Applied source rock geochemistry. In: Magoon, L.B., Dow, W.G. (Eds.), The Petroleum System-from Source to Trap. AAPG Memoir, pp. 93–120.
- Peters, K.E., Moldowan, J.M., 1993. The Biomarker Guide. Prentice Hal1, Englewood

Cliffs, NJ, p. 363.

- Philp, R.P., Gilbert, T.D., Friedrich, J., 1981. Bicyclic sesquiterpenoids and diterpenoids in Australian crude oils. Geochim. Cosmochim. Acta 45 (7), 1173–1180.
- Requejo, A.G., 1994. Maturation of petroleum source rocks, II. Quantitative changes in extractable hydrocarbon content and composition associated with hydrocarbon generation. Org. Geochem. 21, 91–105.
- Schoell, M., Hwang, R.J., Carlson, R.M.K., Welton, J.E., 1994. Carbon isotopic composition of individual biomarkers in gilsonites (Utah). Org. Geochem. 21 (6–7), 673–683.
- Seifert, W.K., Moldowan, J.M., 1978. Applications of steranes, terpanes and monoaromatics to the maturation, migration and source of crude oils. Geochim. Cosmochim. Acta 42 (1), 77–95.
- Sinninghe Damsté, J.S., Kenig, F., Koopmans, M.P., Köster, J., Schouten, S., Hayes, J.M., de Leeuw, J.W., 1995. Evidence for gammacerane as an indicator of water column stratification. Geochim. Cosmochim. Acta 59, 1895–1900.
- Song, Y., Li, S., 1994. GC/MS study on n-alkanes, alkenes and bicyclic terpanes of *Botryococcus braunii* with different growing periods. J. Chin. Mass Spectrom. Soc. 15 (4), 16–27 (in Chinese with English abstract).
- Street, J.H., Anderson, R.S., Paytan, A., 2012. An organic geochemical record of Sierra Nevada climate since the LGM from Swamp Lake, Yosemite. Quat. Sci. Rev. 40 (27), 89–106.
- ten Haven, H.L., Rohmer, M., Rullkötter, J., Bisseret, P., 1989. Tetrahymanol, the most likely precursor of gammacerane, occurs ubiquitously in marine sediments. Geochim. Cosmochim. Acta 53, 3073–3079.
- Tissot, B.P., Welte, D.H., 1984. Petroleum Formation and Occurrence, second ed. Springer-Verlag, Berlin, p. 699.
- Trindade, LA.F., Brassell, S.C., 1992. Geochemical assessment of petroleum migration phenomena on a reginal scale: case studies from Brazilian marginal basins. Org. Geochem. 19, 13–27.
- Venkatesan, M.I., 1989. Tetrahymanol: its widespread occurrence and geochemical significance. Geochem. Cosmochim. Acta 53, 3095–3101.
- Volkman, J.K., 2014. Acyclic isoprenoid biomarkers and evolution of biosynthetic pathways in green microalgae of the genus *Botryococcus*. Org. Geochem. 75, 36–47.
- Wang, D.Y., Xin, B.S., Yang, H., Fu, J.H., Yao, J.L., Zhang, Y., 2014. Zircon SHRIMP U-Pb age and geological implications of tuff at the bottom of Chang-7 Member of Yanchang Formation in the Ordos basin. Sci. China Earth Sci. 57 (12), 2966–2977.
- Wang, T., 1990. Approach to Biomarker Geochemistry. China University of Geosciences Press, Wuhan, China, pp. 1–154 (in Chinese with English abstract).
- Weston, R.J., Philp, R.P., Sheppard, C.M., Woolhouse, A.D., 1989. Sesquiterpanes, diterpanes and other higher terpanes in oils from the Taranaki basin of New Zealand. Org. Geochem. 14, 405–421.
- Williams, J.A., Bjorøy, M., Dolcater, D.L., Winters, J.C., 1986. Biodegradation in South Texas Eocene oils effects on aromatics and biomarkers. Org. Geochem. 10, 451–461.
- Yao, J., Deng, X., Zhao, Y., Han, T., Chu, M., Pang, J., 2013. Characteristics of tight oil in Triassic Yanchang Formation, Ordos Basin. Petrol. Explor. Dev. 40 (2), 161–169.
- Yang, H., Fu, S., Wei, X., 2004. Geology and exploration of oil and gas in the Ordos basin. Appl. Geophys. 1 (2), 103–109.

Yu, J., Yang, Y., Du, J., 2010. Sedimentation during the transgression period in Upper Triassic Yanchang Formation, Ordos Basin. Petrol. Explor. Dev. 37 (2), 181–187.

Zhang, C., Li, S., Yang, J., Yang, S., Wang, J., 2004. Petroleum migration and mixing in the Pearl River Mouth basin, South China Sea. Mar. Petrol. Geol. 21, 215–224.

- Zhang, Z.H., Metzger, P., Sachs, J.P., 2007. Biomarker evidence for the co-occurrence of three races (A, B and L) of *Botryococcus braunii* in El Junco lake, Galapagos. Org. Geochem. 38, 1459–1478.
- Zhu, Y., Weng, H., Su, A., Liang, D., Peng, D., 2005. Geochemical characteristics of Tertiary saline lacustrine oils in the western Qaidam Basin, Northwest China. Appl. Geochem. 20, 1875–1889.
- Zobaa, M.K., Oboh-Ikuenobe, F.E., Ibrahim, M.I., 2011. The Cenomanian/Turonian oceanic anoxic event in the Razzak Field, north Western Desert, Egypt: source rock potential and paleoenvironmental association. Mar. Petrol. Geol. 28 (8), 1475–1482.