Distribution and properties of biomarkers in severely biodegraded crude oil of Gudao reservoir, China

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ABSTRACT

Biodegraded crude oils in China are distributed widely and make up a certain portion of heavy-oil resources. An unresolved complex mixture (UCM) of hydrocarbons was isolated from three biodegraded crude oils in the Gudao reservoir of the Shengli Oilfield, China. The biomarker composition of biodegraded oils was determined using GC–MS technique. The results show that n-alkanes were completely depleted, isoprenoids and diasteranes were almost absent. The hydrocarbons expect for tricyclic terpane, steranes, hopane, were preferentially depleted in saturated fraction. Meanwhile, the 25-norhopane series occurs, indicating that the crude oils experienced severe degradation equivalent to levels 5–6.

Based on biomarker proxies, the depositional environment of the Gudao Oils can be divided into two phases. In the first (GD2-19-55 and GD8-27N12), deposition occurred completely in seawater-dominated oxic to suboxic conditions, with primary input of terrestrial higher plants with an abundant influx of aquatic organisms. The second phase (GD2-7-41, GD-KD-162, GD-KD-18-168 and GD-KD-45) consisted of mainly seawater anoxic to suboxic/oxic conditions along with a small freshwater influence, with diluted organic matte derived from phytoplankton and a lesser influence from terrestrial higher plants. In addition, the vitrinite reflectance (Ro) of ca. 0.73–0.89% and methylphenanthrene index (MPI-1) of ca. 0.55–0.82 indicate the organic matter to be mature.

1. Introduction

After accumulating in the reservoir, the evolution of oil does not stop. Actions such as thermal evolution, oxidation, water washing and bacteria degradation all change the original characteristics of crude oils. Simulation experiments and actual samples demonstrate that the bacteria degradation starts from linear alkanes and branched alkanes, cycloalkanes or aromatics have the ability of anti-biodegradation (Setti et al., 1993; Peters and Moldowan, 1995; Heath et al., 1997). Utilizing GC–MS, we can find out the existing information of biomarkers in various kinds of crude oils and the influence of biodegradation to biomarkers. All these are very meaningful in the aspect of enriching and perfecting the recognition to crude oils.

Petroleum geochemistry studies mainly the chemical compositions, structures and characteristics of biological ashes of natural organisms in earth, the regularities of distribution, evolution and transition of organic matters and their products under different circumstances. Over a long period of time, biomarkers have become the main techniques used in petroleum exploration to study oils, in particular their origin and maturity, oil to source rock and oil to oil correlations (Pieri et al., 1996; Bost et al., 2001; Wenger and Isaksen, 2002; Huang et al., 2004; Hao et al., 2009) since they are widely distributed and easily detected by conventional gas chromatography-mass spectrometry (GC–MS).

Heavy oil is an important component of global oil resources. Current estimates indicate that heavy oil is up to ten times more abundant than conventional oil. Meanwhile, heavy oils in China are distributed widely and abundant. It is estimated that the undiscovered heavy oil resources are 25 billion tons in China (Niu and Hu, 1999), indicating that the potential of heavy oil resources is great.

Shengli Oilfield is the second largest oil-producing base in Shandong Province, NE China. It is a large scale Cenozoic petroliferous basin and its main body lies in the Yellow River Delta. There has been more than 40-yr history of exploration and exploitation in Shengli Oilfield. Nowadays, with the development of oil production and appearance of new situations, there are many new problems to be solved in exploration and exploitation. Biomarker is one of the powerful tools to better understand the origin and occurrence of biomarkers compositions in crude oils, source rocks and oil reservoirs. That is favorable for revealing the mechanism of oil formation, exploiting new oil reservoirs, reducing operation costs and improving oil production (Leontaritis, 1996; Moumouni et al., 2007; Zhang et al., 2008). Furthermore, since oils vary considerably in properties, they also vary in economic value. Patterns of oil quality are commonly

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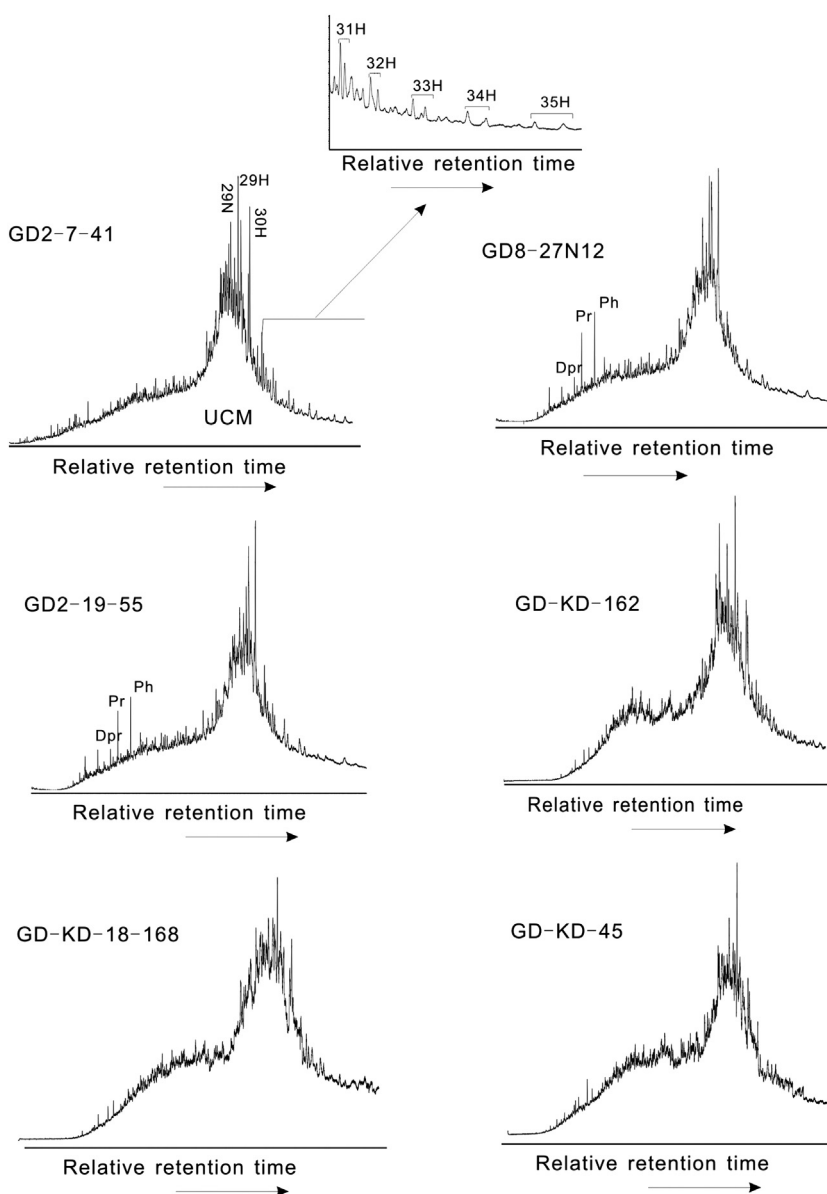E-mail addresses: yqxia@lzb.ac.cn (Y. Xia), wyll6800@lzb.ac.cn (Y. Wang).

Fig. 1. GC–MS Chromatogram of saturate fraction for crude oils from Gudao reservoir of Shengli Oilfield. Abbreviations: 29N=17α,21β-25-norhopane, 29H=17α,21β-30-norhopane, 30H=17α,21β-hopane.

controlled by the various processes of maturation and alteration, and are predictable from a knowledge of theses degradation processes. As a result, analysis of the distribution and properties of biomarkers in severely biodegraded crude oil could be developed as a possible proximity indicator.

In this study, on the basis of a GC–MS method for biomarkers in crude oils, representative samples according to biodegradation in Gudao reservoir of Shengli Oilfield of eastern China were analyzed. Some interesting distribution regularities of biomarkers were summarized. The distribution and properties of biomarkers and rational deduction on their ability of anti-biodegradation were discussed.

2. Experimental

2.1. Samples and analytical methods

The sample suite comprises severe progressively biodegraded crude oils from the Gudao reservoir of Shengli Oilfield located in the Hekou district of the city of Dongying, Shandong Province, NE China. The depth of oil production is from 1120 to 1350 m in the reservoir. The crude oil of the Gudao reservoir is of higher density, viscidity and colloid, lower wax freezing point, and belongs to the typical heavy oil type.

Asphaltenes were removed by precipitation with n-hexane followed by filtration. The de-asphaltened oils were then separated into saturate, aromatic and polar fractions using column chromatography with a mixture of pre-activated silica gel and alumina (4:1, v/v) as stationary phase, with n-hexane, Dichloromethane, and methanol as eluents, respectively.

2.2. GC–MS analysis

GC–MS analysis was performed using a Hewlett-Packard 6890 gas chromatograph (GC) coupled to a Hewlett-Packard 5973 mass selective detector (MSD). The GC was fitted with a HP-5 capillary column (30 m×0.25 mm×0.25 μm, Agilent, USA). The oven temperature was programmed from 80 to 280 °C at 3 °C/min with
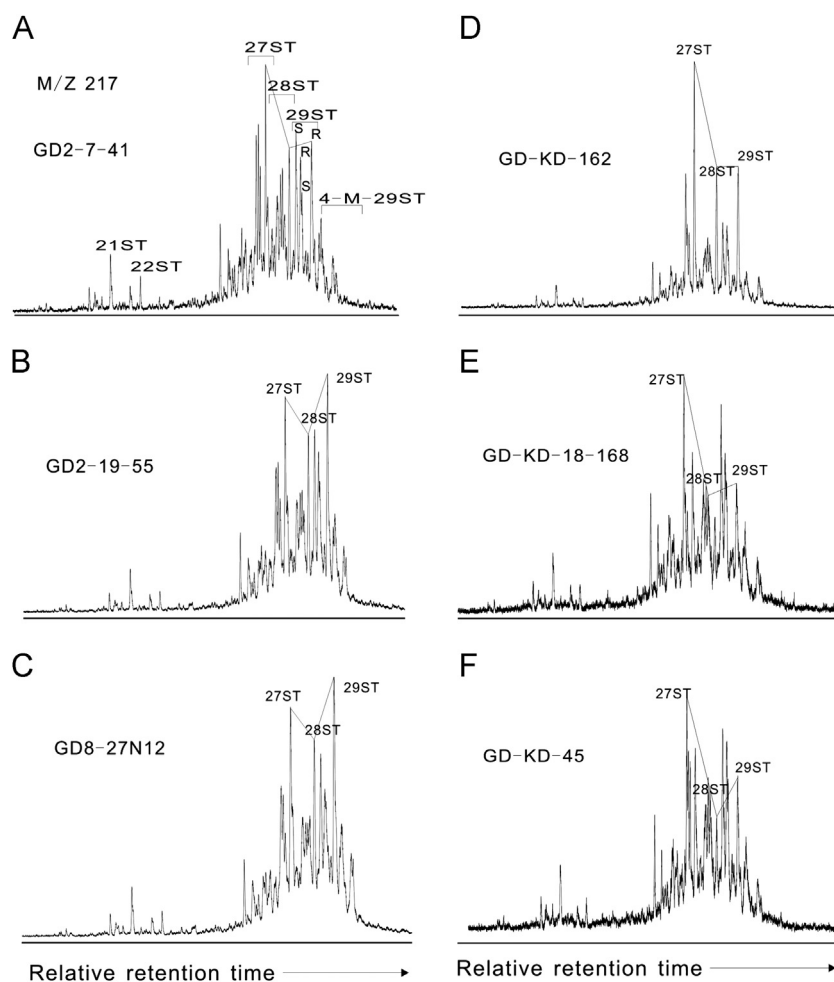
Fig. 2. Representative m/z 217 mass fragmentograms showing the steranes distribution in the studied oils from the Gudao reservoir of Shengli Oilfield. Abbreviations: 27St = 27$\alpha\alpha\alpha$R + S + 27$\alpha\beta\beta$R + S, 27$\alpha\alpha\alpha$S = 5α,14α,17α-20S-cholestane, 28$\alpha\beta\beta$S = 5α,14β,17β-20S-24-methylcholestane, 29$\alpha\beta\beta$R = 5α,14β,17β-20R-24-ethylcholestane, 21St = 5α,14β,17β-pregnane, 22St = 5α,14β,17β-20-methylpregnane.

initial and final hold times of 1 and 30 min, respectively. Helium was used as the carrier gas at a linear velocity of 28 cm/sec, with the injector operating at constant flow of 0.9 ml/min. The MSD was operated with an ionization energy of 70 eV, a source temperature of 230 °C and an electron multiplier voltage of 1800 V over the mass range 35–550 amu. Data collected in either the full-scan or selected ion monitoring (SIM) mode.

3. Results and discussion

3.1. Saturated hydrocarbons

The gas chromatogram of saturate fraction of Gudao reservoir crude oils (Fig. 1) reveals several diagnostic features. The n-alkanes have been completely removed, and some acyclic isoprenoids are being destroyed and traces of 25-norhopanes are present, indicating that the oils of GD2-19-55 well and GD8-27N12 well are moderately to severely biodegraded (PM 5–6), whereas at the oils of GD2-7-41 well, GD-KD-162 well, GD-KD-18-168 well, and GD-KD-45 well, n-alkanes and acyclic isoprenoid alkanes have been completely removed, hopanes are being destroyed, and traces of 25-norhopanes are present, indicating a petroleum degradation level of PM 6 (Peters and Moldowan, 1995). Other biodegradation products, the 25-norhopanes, are found in the two fields of GD2-19-55 well and GD8-27N12 well. Their occurrence is

probably due to mixing of severely biodegraded oil residues with moderately biodegraded crude oils during accumulation in the reservoirs. Furthermore, it appears as a pronounced rising baseline in the chromatogram. There is an obvious UCM hump in the saturate fraction, as shown in Fig. 1. There are some complex mixtures, which is insufficient to be resolved by GC–MS. The number of unidentified compounds comprising such UCM may amount to 250,000 compounds (Sutton et al., 2005), indicating that an enormous amount of inaccessible, geochemical information is unexploited.

3.1.1. Steranes and terpanes

The distribution of steranes (m/z 217) and terpanes (m/z 191) as obtained by the GC–MS analysis of alkanes are given in Figs. 2 and 3, respectively. Almost all of the oils studied contain abundant steranes with seldom diasteranes (Fig. 2). The distribution of C_{27}, C_{28} and C_{29} steranes is "L" shaped (e.g. GD2-7-41, GD-KD-162, GD-KD-18-168, and GD-KD-45, C_{27}–C_{29} with $C_{27} > C_{29} > C_{28}$, Fig. 2) and asymmetrical "V"-type distribution (e.g. GD2-19-55 and GD8-27N12, C_{27}–C_{29} with $C_{29} > C_{27} > C_{28}$, Fig. 2). The C_{27} steranes derive mainly from phytoplankton, whereas C_{28} steranes often originate from specific phytoplankton types (e.g. diatoms; Volkman et al., 1998) and C_{29} steranes from terrestrial higher plants (e.g. Volkman, 1986). Furthermore, C_{27} and C_{28} steranes may also originate from algae within lacustrine or swamp environments
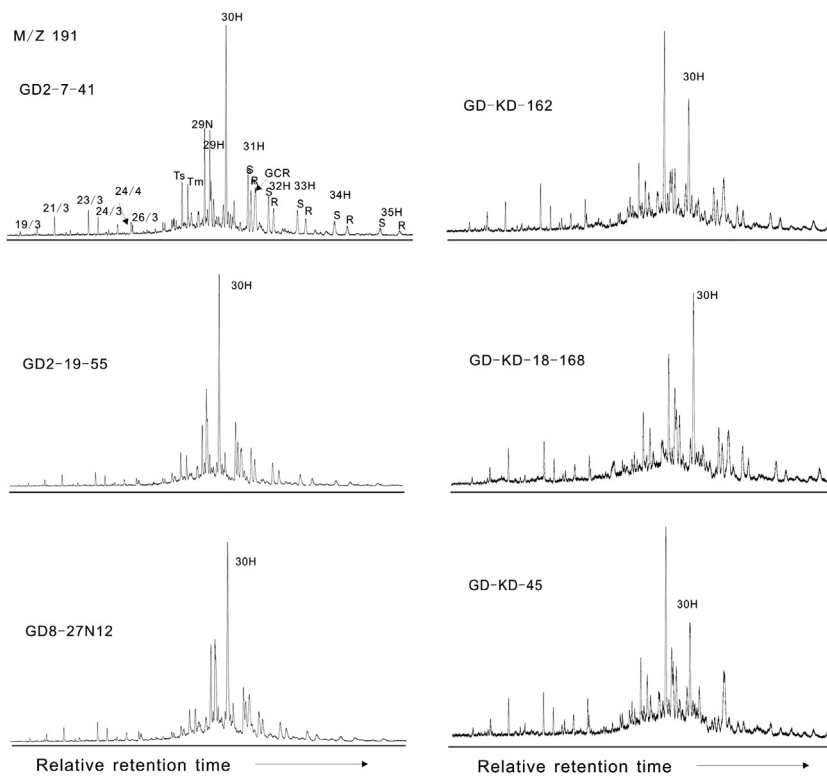
Fig. 3. Representative *m/z* 191 mass fragmentograms showing the terpanes distribution in the studied oils from the Gudao reservoir of Shengli Oilfield. Abbreviations: 23/3=C$_{23}$ tricyclopolyprenane, Ts=18α-22,29,30-trisnorneohopane, Tm=17α-22,29,30-trisnorhopane,29H=17$\alpha\beta$,21β-30-norhopane,30H=17α,21β-hopane,31HS=17α,21β-22S-30-homohopane,35HS=17α,21β-22S-29-pentakishomohopane,GCR=gammacerane.

Table 1
Selected geochemical parameters for the crude oils from Gudao of Shengli Oilfield.

Well	Ts	C$_{29}$ $\alpha\beta$	C$_{30}$ $\alpha\beta$	S/(S+R)	C$_{29}$ $\beta\beta$	C$_{29}$ 20S	(P+AP)/(C+MC)	C/MC	(C+MC)/T	(C$_{26}$+C$_{27}$)/C$_{28}$	C$_{26}$/C$_{28}$	C$_{27}$/C$_{28}$	MPI-1	%Rc
GD2-7-41	0.52	0.77	0.88	0.59	0.43	0.46	0.57	0.45	0.26	1.8	0.88	1.05	0.82	0.89
GD2-19-55	0.54	0.81	0.89	0.61	0.41	0.40	0.98	0.54	0.36	2.1	0.68	1.08	0.69	0.82
GD8-27N12	0.52	0.84	0.87	0.59	0.40	0.36	1.24	0.58	0.38	1.9	0.67	1.04	0.55	0.73
GD-KD-162	0.61	0.93	0.85	0.59	0.35	0.34	–	0.62	0.17	2.2	1.03	1.09	–	–
GD-KD-18-168	0.62	0.90	0.88	0.61	0.42	0.51	–	0.76	0.33	2.2	1.25	1.09	–	–
GD-KD-45	0.60	0.91	0.74	0.57	0.45	0.48	–	0.56	0.36	2.1	1.01	1.05	–	–

Ts=Ts/(Ts+Tm); C$_{29}$ $\alpha\beta$=C$_{29}$ $\alpha\beta$ hopane/(C29 $\alpha\beta$ hopane+C$_{29}$ $\beta\alpha$ hopane); C$_{30}$ $\alpha\beta$=C$_{30}$ $\alpha\beta$ hopane/(C$_{30}$ $\alpha\beta$ hopane+C$_{30}$ $\beta\alpha$ hopane); S/(S+R)=C$_{31}$ $\alpha\beta$ hopanes (22S/(22S+22R)); C$_{29}$ $\beta\beta$=C$_{29}$ $\beta\beta$/($\alpha\alpha$+$\beta\beta$) steranes; C$_{29}$ 20S=C$_{29}$ $\alpha\alpha\alpha$ 20S/(20S+20R) steranes; (C$_{26}$+C$_{27}$)/C$_{28}$=(C$_{26}$ triaromatic steroid hydrocarbons+C$_{27}$ triaromatic steroid hydrocarbons)/ C$_{28}$ triaromatic steroid hydrocarbons; C$_{26}$/C$_{28}$=C$_{26}$/C$_{28}$ 20S triaromatic steroids ratio; C$_{27}$/C$_{28}$=C$_{27}$/C$_{28}$ 20R triaromatic steroids ratio; (C+MC)/T=(chrysene+methylchrysenes)/triaromatic steroid hydrocarbons; (P+AP)/(C+MC)=(phenanthrene+alkyl-phenanthrenes)/(chrysene+methyl-chrysenes); C/MC=chrysene/methyl-chrysenes; MPI-1=methylphenanthrene index-1 (1.5×[3–MP+2–MP]/[P+9–MP+1–MP]); %Rc=calculated vitrinite reflectance from MPI-1 (0.6×MPI-1+0.4) (Radke and Welte, 1983).

(Volkman, 2003; Piedad-Sánchez et al., 2004). The distribution in Fig. 2 indicates that the organic matter in the Gudao crude oils is of diverse origins. The distribution of types C$_{27}$–C$_{28}$–C$_{29}$ steranes (Fig. 2) suggests that in the crude oils of GD2-7-41, GD-KD-162, GD-KD-18-168 and GD-KD-45 it was derived from aquatic organisms and a lesser influence from terrestrial higher plants, whereas that in the GD2-19-55 and GD8-27N12 originated mainly from terrestrial higher plants with a abundant influx of aquatic organisms (Peters and Moldowan, 1995).

The GC–MS ion chromatograms of the aliphatic fractions (Fig.3) clearly indicate the presence of hopanes, with the C$_{29}$–C$_{35}$ hopane. The 22S/(22S+22R) ratio of 17α(H), 21β(H)-homohopanes is showed between 0.57 and 0.61 for six crude oils (Table 1). These ratios are close to equilibrium ratio of 0.6 in mature oils and indicate the Gudao oils were in stage of maturity (Peters and Moldowan, 1995). The GC–

MS chromatograms (Fig.3) also contain peaks of tricyclic terpanes (C$_{19}$–C$_{26}$) (Aquito Neto et al., 1983), especially in the GD2-7-41, GD-KD-162, GD-KD-18-168, and GD-KD-45 crude oils, and a peak of a C$_{24}$ tetracyclic terpane in all oils, maximizing at C$_{23}$ (abbreviated as 23/3). The distributions of tricyclic terpanes in all of the studied oils are usually C$_{19}$<C$_{20}$<C$_{21}$<C$_{23}$ (Fig. 3), typical of Chinese lacustrine oils (Shi et al., 2005), indicating possible inputs from prokaryotic membranes for the Zhanhua Depression oils.

In addition, hopane distributions are characterized by low amounts of Ts and Tm, with Ts/(Ts+Tm) close to 0.5 (Table 1; Fig. 3), and relatively high gammacerane abundances (Fig. 3). The Ts/(Ts+Tm) values in all oils are mostly equal (Table 1), suggesting both suboxic and oxic conditions prevailed during their deposition (Waseda and Nishita, 1998). Gammacerane is thought to originate from phototrophic bacteria, which are generally abundant
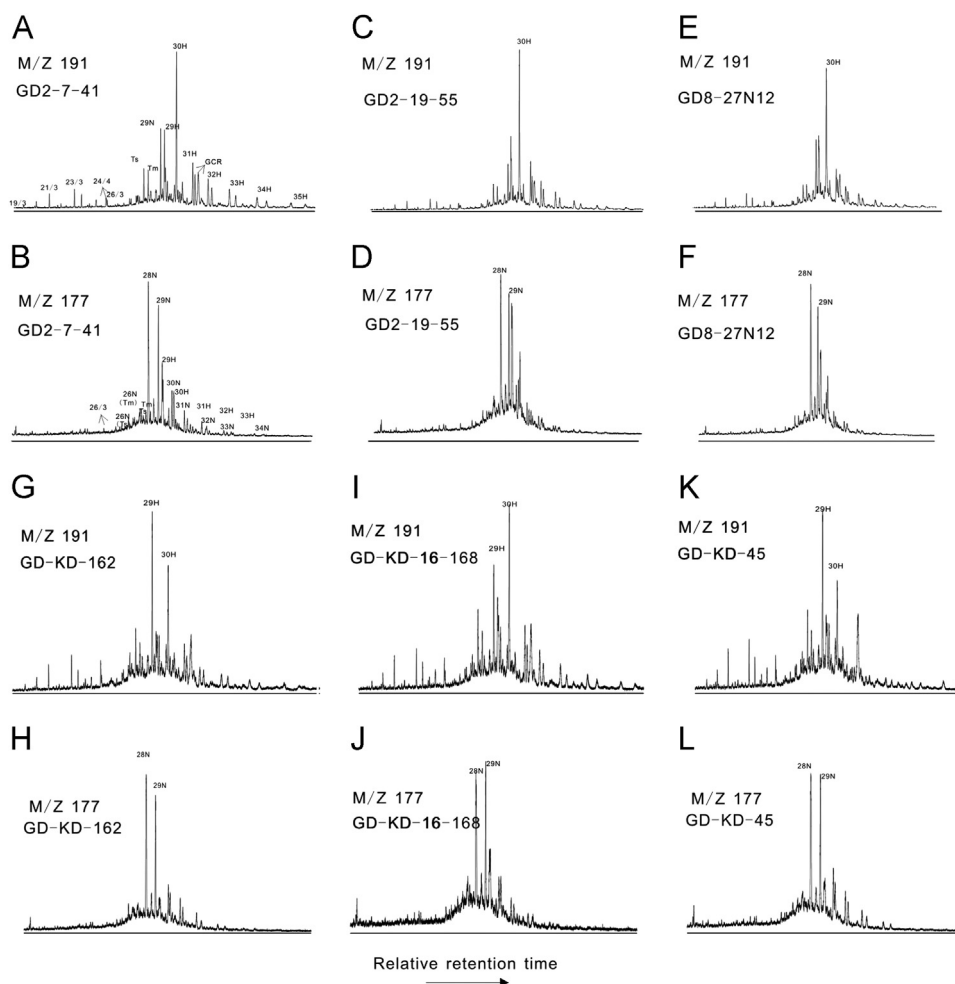
Fig. 4. Mass chromatograms m/z 191 (top) displaying degraded hopanes and m/z 177 (bottom) displaying demethylated hopanes in three severely biodegraded oils samples from Gudao of Shengli Oilfield. Homologous series of 25-norhopanes and hopanes having 17α (H) stereochemistry are denoted by the carbon number followed by the letter N and H, respectively. The two commonly occurring trisnorhopanes are designated Ts and Tm, while the demethylated compounds are labeled as 26N. GCR=gammacerane. 23/3=C_{23} tricyclopolyprenane, 24/4=de-E-hopane.

in saline lake environments. Large quantities of gammacerane are, therefore, often associated with stratified water columns, possibly saline and reducing conditions during deposition of the organic matter. All the crude oils with high gammacerane and high steroid contents, low content of diasteranes probably belong to the same genetic family.

3.1.2. 25-Norhopanes

From the analysis of the m/z 177 fragmentograms (Fig. 4), it can be seen that there are apparent compounds of 28N and 29N (25-norhopanes). Furthermore, we can see an integrated pair peak of C_{30}–C_{34} norhopane from the enlarge Chromatogram. There is general agreement that these compounds are a series of pound biodegraded by C_{29}–C_{35} hopane. In the corresponding m/z 177 chromatogram, the demethylated counterparts of Ts and Tm are observed (Fig. 4). The occurrence of 25-norhopanes in the crude oil also indicated that the reservoir has experienced at least heavy (PM5-6) biodegradation (Bennett et al., 2006).

The origin of 25-norhopanes in crude oils remains controversial. Some workers suggest that nonbiodegraded oils are concentrated during biodegradation because 25-norhopanes are more resistant to microbial attack than many other compounds (Blanc and connan, 1992). However, we agree with others that microbial demethylation of extended 17α, 21β (H)-hopanes to 25-norhopanes occurs mainly

during biodegradation of petroleum in reservoirs (Moldowan and McCaffrey, 1995; Alberdi et al., 2001; Tocco and Alberdi, 2002; Bennett et al., 2006). Because the distribution of 25-norhopanes in nonbiodegraded lipids typically consist of only one of a few compounds rather than the complete suite of 25-norhopanes observed in crude oils (Moldowan and McCaffrey, 1995). Similarly, other investigators have observed the complete suite of 25-norhopanes in heavily degraded reservoir oils (e.g. Requejo and Halpern, 1989; Moldowan et al., 1995; Bennett et al., 2006). Therefore, the phenomenon indicates that degradation of petroleum in Gudao reservoirs is caused by microbe rather than water-washing or others nonbiodegraded results. Furthermore, the 17β(H), 21β(H) stereochemistry is a thermally unstable biologically-derived structure, suggesting that the 17β(H), 21β(H) 25-norhopanes may derive from petroleum-degrading microbes rather than representing a direct input, we propose that demethylation of 17β(H), 21β(H) hopanes derived from bacteria in the reservoir may give rise to 17β(H), 21β(H) 25-norhopanes, implying that microbial reworking of biomass is occurring alongside petroleum degradation. In addition, 25-norhopanes have been observed in petroleum reservoirs where the hopanes are demethylated prior to sterane alteration (Brooks et al., 1988). However, if the sterane are degraded prior to the hopanes, then the 25-norhopanes are not formed (Seifert and Moldowan, 1979). From the Fig. 4, we can see the 25-norhopanes, implying that the hopanes are demethylated prior to sterane alteration in the crude oils of Shengli oilfield.
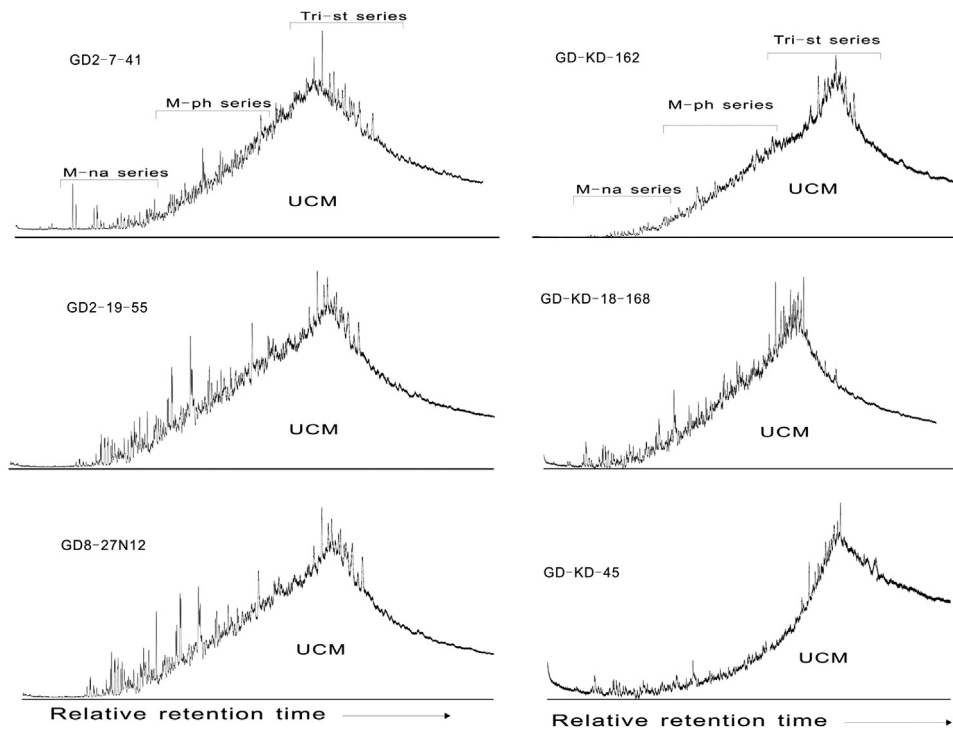
Fig. 5. GC–MS Chromatogram of aromatic fraction for crude oils from Gudao reservoir of Shengli Oilfield. Abbreviations: M-na series=methylnaphthalenes, M-ph series=methylphenanthrenes, Tri-st series=triaromatic steroids.

3.2. Aromatic hydrocarbons

The gas chromatograms of aromatic fraction of Gudao reservoir crude oils are given in Fig. 5. In this study we found that there are also severe biodegradation of aromatic fraction which results a pronounced rising baseline and an obvious UCM hump in the chromatogram. The hydrocarbons expect for triaromatic steranes, few methylnaphthalenes, methylphenanthrenes and chrysene series were completely depleted in aromatic fractions, indicating that severe biodegradation has experienced in the six crude oils of Gudao reservoir. Since previous researches have shown that biodegradation can change the composition of crude oils and cause the large quantity of aromatic fractions degraded (Seifert, 1979; Jones el al., 1983; Lafargue and Barker, 1988).

3.2.1. Phenanthrene and chrysene series

Fig. 6 shows distribution of alkyl-phenanthrenes for oils with different biodegradation levels from six wells (GD2-7-41, GD2-19-55, GD8-27N12, GD-KD-162, GD-KD-18–168 and GD-KD-45) in Gudao Shengli Oilfield. A domination of phenanthren and methyl-phenanthrenes in the alkyl-phenanthrenes of the moderately biodegraded oil from GD8-27N12 well, A domination of methyl- and dimethyl-phenanthrenes from GD2-19-55 well, and a domination of C_2- and C_3-phenanthrenes in the alkyl-phenanthrenes of the severely biodegraded oil from GD2-7-41 well are revealed in Fig. 6. In contrast, at the oils of GD-KD-162 well, GD-KD-18–168 well and GD-KD-45 well, except a small amount of phenanthrene, alkyl-phenanthrenes almost have been completely removed (Fig. 6), indicating the oils could have been severely biodegraded and that is not washed. Because an experimental investigation has been carried out by de Hemptinne et al., 2001. They concluded on a disappearance of the light aromatic compounds prior to heavy aromatic compounds when the oil had been washed by a large amount of water.

MPI-1 index is used to identify maturity of oil and the organic matter (Radke and Welte, 1983; Zakir Hossain et al., 2009). The methylphenanthrene isomers 2-MP and 3-MP (β-isomers) are thermodynamically more stable than 1-MP and 9-MP (α-isomers) isomers (Radke and Welte, 1983; Zakir Hossain et al., 2009). The MPI-1 values and Ro values were calculated out only for the three samples (GD2-7-41, GD2-19-55 and GD8-27N12). The values of MPI-1 and Ro were 0.55% and 0.73% (GD8-27N12), 0.69% and 0.82% (GD2-19-55), and 0.82% and 0.89% (GD2-7-41), respectively (Table 1), suggestive of moderate maturity (Radke and Welte, 1983).

Chrysene series compounds have one more aromatic cycle and stronger resistance to biodegradation than phenanthrene series compounds. This conclusion is proven by the ratios of (phenanthrene+methyl-phenanthrenes)/(chrysene+methyl-chrysenes) for the oils from wells in the Gudao area. The ratios change from 1.24 for the GD8-27N12 well to 0.57 for the GD2-7-41 well (Table 1). Moreover, in the chrysene series, chrysene is more susceptible to biodegradation than methyl-chrysenes. For example, the ratio of chrysene to methyl-chrysenes changes from 0.45 to 0.76 in all oil samples (Table 1). Therefore, in the alkyl-chrysene series, the resistance to biodegradation increases with increasing number of methyl-substituents and with increasing alkyl-chain length.

3.2.2. Triaromatic steroid hydrocarbons

The triaromatic steroids were detected on m/z 231 mass chromatograms of aromatic fractions of oils extracts. Because C_{26}–C_{28} 20R homologs cannot be directly compared on this chromatogram due to co-elution of C_{26} 20R with C_{27} 20S, an alternative approach is applied comparing C_{27} 20R with C_{28} 20R and C_{26} 20S with C_{28} 20S homologs. In Gudao oils, most of oil samples contain higher C_{27} 20R and C_{26} 20S triaromatic steroids relative to C_{28} isomers (Fig. 7) and the values of C_{26}/ C_{28} 20S (0.67–1.25) and C_{27}/ C_{28} 20R (1.04–1.09) in all oil samples are >0.30 and
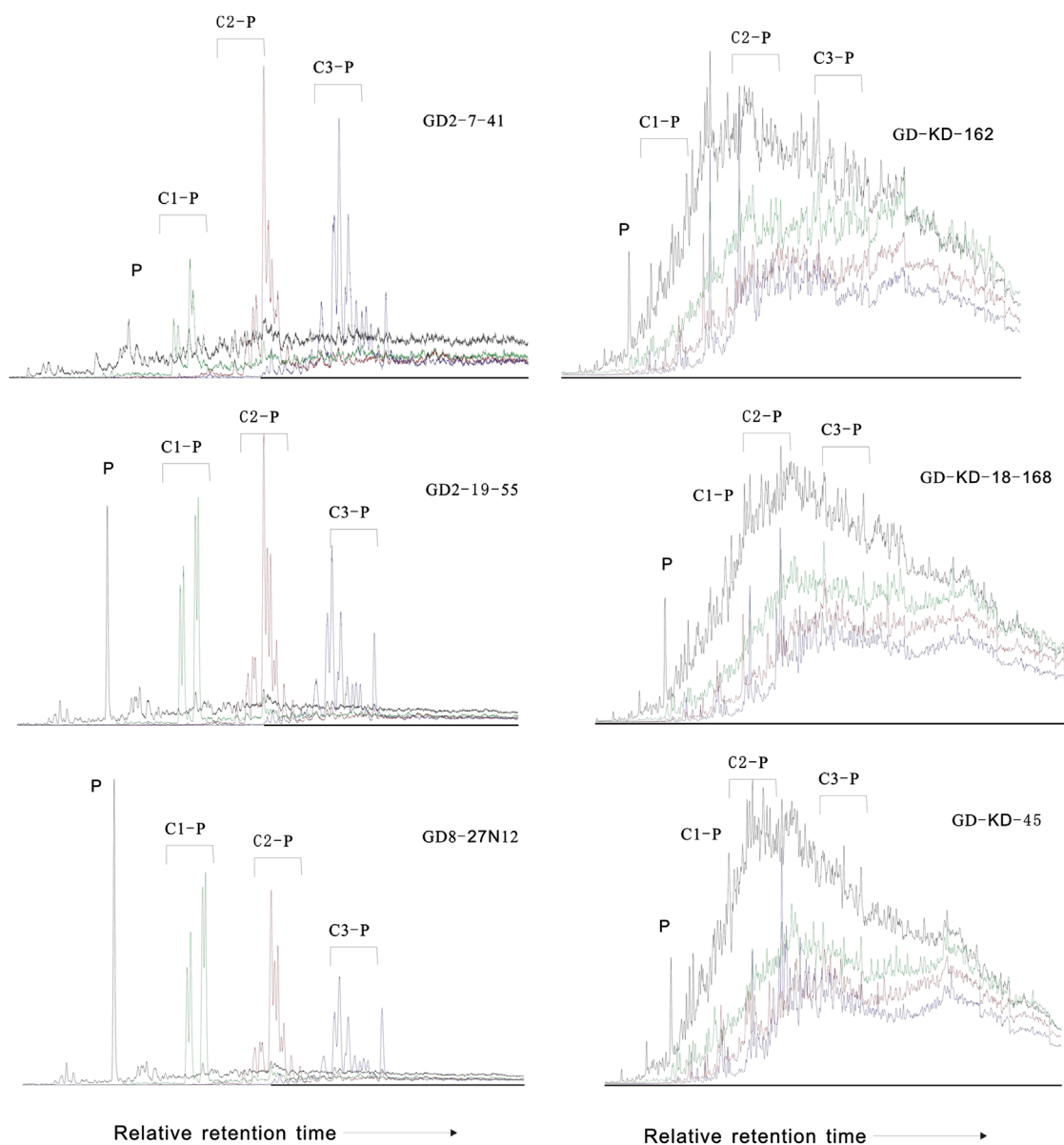
Fig. 6. Mass spectrogram (m/z=178, 192, 206, 220) showing alkyl-phenanthrene series in three crude oils (aromatic fraction GC–MS SIM analysis) from Gudao reservoir of Shengli Oilfield. Abbreviations: P=phenanthren, C1-P=methyl-phenanthrenes, C2-P=dimethyl-phenanthrenes, C3-P=trimethyl-phenanthrenes.

>0.60 (Table 1), respectively. It shows a characteristic that the severely biodegraded crude oils of Gudao oilfield derived from the carbonate in the Upper part of Shahejie-4 (Es4) and mud rock in the lower part of Shahejie-3 (Es3). However, the oil reservoirs were Ordovician limestone (Wang, 2011).

Furthermore, the triaromatic steroid $(C_{26}+C_{27})/C_{28}$ ratios for the oils lie between 1.8 and 2.1. It shows that the oils are not only generated from the same source rocks, but also that serious biodegradation have no effect on the triaromatic steroid hydrocarbons (Fig. 7). In addition, the ratios of (chrysene+methyl-chrysenes)/ triaromatic steroid hydrocarbons (m/z 231) range from 0.38 for the GD2-19-55 well to 0.17 for the GD-KD-162 well (Table 1). Namely, triaromatic steroid hydrocarbons are relatively more stable than the chrysene series. As a result, we can also conclude that the progressive sequence of the resistance of polycyclic aromatic hydrocarbons to biodegradation is triaromatic steroid hydrocarbons, chrysene series and phenanthrene series (Niu, 1990). Furthermore, the result also indicated that the triaro-matic steroid hydrocarbons are little affected by the microbial

degradation and therefore can be used to correlate biodegraded oils with related, unaltered oils and source rocks and to assess the depositional environments of the source rocks for those severely biodegraded oils.

4. Conclusions

The crude oil samples indicate extremely high degradation of oil hydrocarbons, evidenced by a complete loss of n-alkanes, almost absent isoprenoids and by the occurrence of obvious "UCM" humps in the saturate fraction and aromatic fraction. The presence of 25-norhopanes indicated that the crude oil samples accumulation have experienced at least heavy (PM 5-6) biodegradation and the hopanes are demethylated prior to steranes alteration in the Gudao crude oils.

The geochemical data shows that the progressive sequence of resistance of polycyclic aromatic hydrocarbons to biodegradation is triaromatic steroid hydrocarbons, chrysene series and phenanthrene
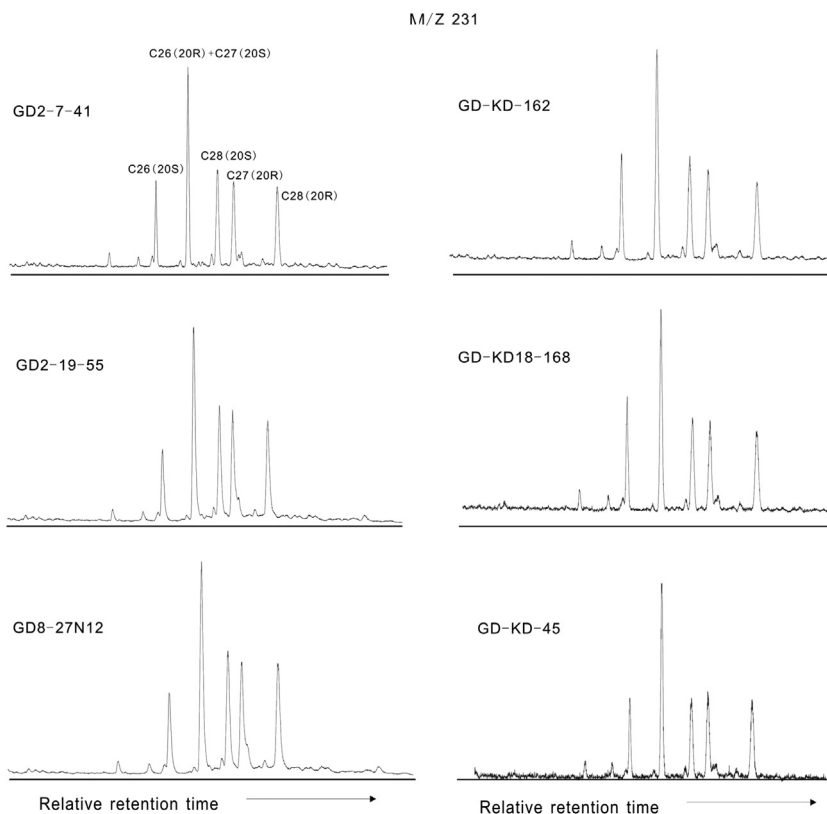
Fig. 7. Mass spectrogram of triaromatic steroid ($m/z=231$) for crude oils from Gudao reservoir of Shengli Oilfield.

series. In the alkyl-chrysene series, the resistance to biodegradation increases with increasing number of methyl-substituents and with increasing alkyl-chain length.

The sterane and hopane compositions, and also Ts/(Ts+Tm) ratio values suggest that the Gudao crude oils were deposited in two main phases. In the first (GD2-19-55 and GD8-27N12), higher plant organic matter with abundant aquatic organisms was deposited in seawater-dominated, oxic to suboxic conditions. In the second phase (GD2-7-41, GD-KD-162, GD-KD-18-168 and GD-KD-45), planktonic organic matter was deposited mainly in seawater influenced, oxygen-poor freshwater conditions, with some transitions between anoxic and suboxic/oxic environments.

All oil samples contain higher C27 20R and C26 20S triaromatic steroids relative to C28 isomers with a C26/ C28 20S and C27/ C28 20R ratio of >0.30 and 0.60, respectively, indicating that the severely biodegraded crude oils of Gudao oilfield in the Ordovician reservoirs were likely derived from the carbonate in the Upper part of Shahejie-4 (Es4) and mud rock in the lower part of Shahejie-3 (Es3). According to the 22S/ (22S+22R) homohopane ratios, the MPI-1 index and Ro maturity parameters, the Gudao oils are of mature.

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