

Mixing and biodegradation of hydrocarbons in the Daerqi oilfield, Baiyinchagan Depression, northern China

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Abstract

Crude oils in the Daerqi oilfield vary greatly in viscosities, including normal, viscous and highly viscous oils. They are also dramatically different in thermal maturity, from immature to mature based on biomarker parameters. According to bulk and molecular geochemical characteristics, crude oils can be classified into three groups in this oilfield. Group I oils are mature and derived from the deeply buried and relatively old source rocks within the Tengger Formation and the second member of the Arshan Formation of early Cretaceous age. Group II oils are immature to marginally mature and derived from the relatively young source rocks that experienced shallow burial within the first member of the Duhongmu Formation of earlier Cretaceous age. Group III oils are mixtures of group I and group II oils, with dominance of the group I oils (>70%). The viscosity is low for the non-biodegraded group I and group III oils (7.1–24 mPa s) but very high for the non-biodegraded group II oils (e.g., 433,104 mPa s for the representative oil Da12O1). The group III oils are similar to the group I oils in gross properties (e.g., gross composition and viscosity), but are similar to group II oils in terms of their molecular maturity parameters. The oil reservoirs are currently at a shallow depth (<800 m), and some oils are heavily biodegraded up to level 4 on the [Peters, K.E., Moldowan, J.M., 1993. *The Biomarker Guide: Interpreting Molecular Fossils in Petroleum and Ancient Sediments*. Englewood Cliffs, Prentice-Hall, NJ] scale in this oilfield. A peculiar phenomenon is that some of the group I and group III oils have been heavily biodegraded, whereas the group II oils, interbedded with the biodegraded group I and/or group III oils within a narrow interval in the same wells, are not altered by biodegradation. This is possibly due to the low diffusion coefficient of hydrocarbons and isolation to meteoric water percolation for the group II oil columns.

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1. Introduction

Numerous studies have documented the mixing of oils in reservoirs from different source rocks or

from a same source rock but with substantial maturity variations (e.g. England, 1990; Larter and Aplin, 1995; Rooney et al., 1998; Scotchman et al., 1998; Dzou et al., 1999; Pan and Yang, 2000; Jiang et al., 2001; Li et al., 2001, 2003; Jiang and Li, 2002a,b; Chen et al., 2003a,b; Pan et al., 2003, 2005; Pang et al., 2003; Zhang et al., 2003;

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Wilhelms and Larter, 2004; Arouri and McKirdy, 2005). However, the mixing phenomenon is not easy to recognize in some reservoirs using routine molecular parameters. If one oil (oil A) is mixed with another oil (oil B) which contains biomarker compounds (steranes and terpanes) in concentrations of one-tenth to even 1% of those in oil A, the mixed oil will exhibit the molecular characteristics of oil A, but will have no sign of oil B even though it may be dominated by oil B (>50%). These types of mixed oils have been observed in oil pools in the eastern Pearl River Mouth Basin by Zhang et al. (2003). Moreover, if this type of mixed oil is biodegraded heavily with terpanes and steranes dominating in the saturated fraction, the determination of oil sources can be more difficult. This complicated issue is encountered in the present study.

The Daerqi oilfield is located on the south slope of the Baiyinchagan Depression (Fig. 1a). Since the first commercial oil well (well Da2) was drilled in 1994, about 130 million barrels of original oil-in-place (OOIP) have been found in this oilfield (Wang et al., 1999). The physical properties and

geochemical characteristics vary dramatically for oils within this oilfield. For example, the non-biodegraded oil from the interval 738.0–748.6 m in well Da2 has a low viscosity and density (7.1 mPa s and 0.84 g/cm³, respectively). However, the non-biodegraded oil from the interval 416.6–424.0 m of well Da12 has a very high viscosity and density (433,104 mPa s and 0.97 g/cm³, respectively). The oil from the interval 356–370.4 m in well Da7, near well Da12 (Fig. 1b), has been heavily biodegraded and has a viscosity and density of 2134 mPa s and 0.92 g/cm³ respectively, relatively higher than the non-biodegraded oil from well Da2, but substantially lower than the non-biodegraded oil from well Da12. There are several problems to be resolved for both the reservoir development and further exploration in this region:

- (1) Are the viscosities and densities of these oils controlled by the kerogen type and maturity of their source rocks, or by alteration during and after oil migration and accumulation?
- (2) How many genetic oil types and source rocks are there in this region?

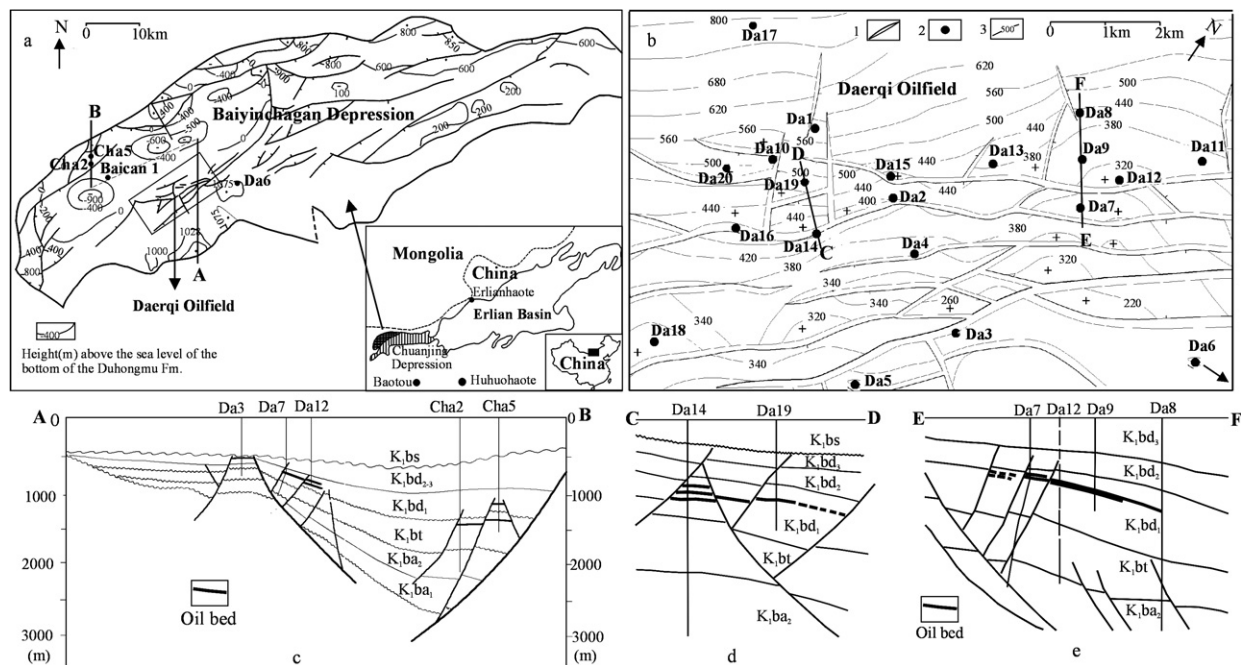


Fig. 1. Location of the Daerqi Oilfield in the Baiyinchagan Depression (a); map of the Daerqi Oilfield, showing the Daerqi wells (b); and three cross sections across the Daerqi Oilfield (c–e). In (b), 1 = fault; 2 = well; 3 = burial depth to the top of the first section of the Duhongmu Formation. In (d), for the cross section of the oil reservoir Da14–Da19, there are three oil columns in the Da14 well. From shallow to deep, the first oil column is a group III oil, the second oil column was not analyzed, and the third oil column is a group I oil. In the Da19 well, the only oil column is a group III oil.

- (3) How can the viscosities of oils in potential exploration targets be predicted?
- (4) How can an estimate be made of the viscosity of an oil column in the Daerqi oilfield, based on some easily obtained geochemical data?

A few previous studies have documented the geochemical and physical properties of oils from Daerqi oilfield (Zhang et al., 1999; Huang et al., 2003). Zhang et al. (1999) believed that the formation of the highly viscous oil (e.g. non-biodegraded oil from well Da12) mainly resulted from oil evaporation after accumulation. Huang et al. (2003) suggested that water-washing could be the primary process leading to the formation of this type of unusual heavy, viscous oil, in combination with evaporation and leakage. As the oil mixing process was not recognized in these previous studies, the previous explanations of the formation of the highly viscous non-biodegraded oils need to be reconsidered.

The effects of biodegradation on the chemical compositions and physical properties have been studied since the early 1970s (e.g. Evans et al., 1971; Bailey et al., 1973; Hunt, 1979; Connan, 1984; Tissot and Welte, 1984; Peters and Moldovan, 1993). Recent studies have shown that petroleum biodegradation occurs most likely under anoxic conditions through anaerobic microbial metabolism (Wilkes et al., 2000, 2003; Head et al., 2003; Larter et al., 2003), rather than under oxic conditions through aerobic mechanisms as previously thought (e.g. Evans et al., 1971; Hunt, 1979). The anaerobic biodegradation rate is generally very low, e.g. around 5–15 Myr is needed to remove the *n*-alkanes from oil (Head et al., 2003; Larter et al., 2003). Wilhelms et al. (2001) proposed a palaeopasteurization model in which some petroleum reservoirs were pasteurized at 80–90 °C during deep burial, deactivating any hydrocarbon-degrading microorganisms present. Oil reservoirs of the Daerqi oilfield, along with the whole Erlian Basin, have been deeply buried and subsequently uplifted at the end of the Early Cretaceous (Gao et al., 1988; Dou et al., 1998; Wang et al., 1999; Huang et al., 2003). The reservoirs are currently at a shallow depth (<800 m). The oils in some reservoirs are heavily biodegraded, while other reservoirs contain oils that are nearly intact. Based on the palaeopasteurization model presented by Wilhelms et al. (2001), it could be suggested that, in this region, the biodegraded reservoirs were buried at temperatures <80–90 °C, whereas the non-biodegraded ones

reached temperatures >80–90 °C before uplift. However, a peculiar phenomenon observed in this oilfield is that the heavily biodegraded oils and the non-biodegraded oils are sometimes interbedded within a narrow interval in the same wells, suggesting a simple palaeopasteurization model is not applicable.

In the present study, we first document the oil groups and their sources, then we investigate the factors that are primarily responsible for the physical properties of these crude oils, and finally, we discuss the possible causes that resulted in the peculiar occurrences of biodegraded and non-biodegraded oils in this oilfield.

2. Geological setting

The Erlian Basin is a Mesozoic continental rift basin covering an area of more than 100,000 km² (Gao et al., 1988; Dou et al., 1998; Wang et al., 1999; Huang et al., 2003). The Baiyinchagan Depression is a subdepression of the Chuanjing Depression, which is located at the western part of the Erlian Basin in the Inner Mongolia Autonomous Region, northern China (Fig. 1). The basement of the Baiyinchagan Depression consists of Paleozoic metamorphic and magmatic rocks (Wang et al., 1999). The sedimentary sequence of the Depression consists of Cenozoic and Cretaceous strata. During the Jurassic Period, the basement began to rift along northeast-southwest faults accompanied by intense volcanic eruptions (Wang et al., 1999). During the early Cretaceous, this region subsided and a widespread lacustrine sedimentary system developed, resulting in source rock deposition. The total thickness of the Lower Cretaceous is over 4000 m in the sedimentary depocenter area of the Baiyinchagan Depression. At the end of the Early Cretaceous, tectonic uplift and erosion occurred over the whole depression. Some sedimentary strata in the border area were completely eroded. Since then, only minor Upper Cretaceous and Cenozoic sediments were deposited in limited areas (Wang et al., 1999).

The Upper Cretaceous Erliandabusu Formation (K2er) with a thickness of 0–75 m contains gray mudstones, pebbled mudstones, thick gray sandstones and conglomeratic sandstones (Fig. 2).

The Lower Cretaceous Saihantala Formation (K1bs), with a thickness 44–281 m, unconformably overlies the Duhongmu Formation and consists of thick, gray, coarse sandstones, conglomeratic

sandstones, sandy conglomerates, thin gray mudstones and carbonaceous mudstones (Fig. 2).

The Lower Cretaceous Duhongmu Formation (K1bd) consists of three members. The youngest, third member (K1bd3), with a thickness of 67–210 m, consists mainly of thick, dark gray mudstones with minor thin, gray sandstones, shales, silty mudstones and dolomitic mudstones. The second member (K1bd2), with a thickness of 56–413 m, contains mainly gray mudstones, shales and oil shales with minor thin, gray silty–fine grained sandstones. The first member (K1bd1), with a thickness of 120–833 m, unconformably overlies the Tengeer Formation and contains gray mudstones, dolomitic mudstones, siltstones and fine sandstones, as well as some fine to medium grained sandy conglomerates at the bottom near the margin of the Depression. The first member contains the richest source rocks and the highest quality reservoir rocks (Fig. 2).

The Tengeer Formation (K1bt) (with a thickness of 91–828 m) overlies the Arshan Formation and consists of gray to purple mudstones and gray siltstones, fine sandstones and pebbly sandstones (Fig. 2). There is a bed of dolomitic mudstone at

the base which is one of the major source rocks of this region. The dolomitic mudstones, which occur both in the Duhongmu Formation (K1bd) and the Tengeer Formation (K1bt), were deposited under saline and semi-saline lacustrine environments (Wang et al., 1999; Zhang et al., 1999).

The Arshan Formation consists of two members. The second (upper) member (K1ba2) (with a thickness of 102–831 m) consists mainly of gray mudstones interbedded with pebbly sandstones and sandy conglomerates. The gray mudstones are also important source rocks. The first (lower) member (K1ba1) unconformably overlies basement rocks and contains mainly pebbly sandstones and sandy conglomerates with minor red mudstones (Wang et al., 1999; Zhang et al., 1999).

3. Samples and experimental

3.1. Samples

A large set of samples, including source rocks, crude oils and oil-saturated sandstone sidewall cores, were analyzed for gross and molecular com-

Stratigraphy		Sedimentary Facies	Lithology	lacustrine evolution	Source Rocks	Reservoir Rocks
Upper Cretaceous	Erliaandabusu Fm. (Kzer)	Fluvial Facies	Pebbly Mudstones Pebbly Sandstones	withdrawal expansion		
	Saihantala Fm. (K1bs)		Non-grained Pebbly Sandstones			
Lower Cretaceous	Duhongmu Fm. (K1bd)	Deep Water Lacustrine Facies	Mudstones			○
			Mudstones Shales			○
			Oil Shales Mudstones Dolomitic Mudstones		●	○
	Tengeer Fm. (K1bt)	Braided River Delta-Fan Delta- Alluvial-Lacustrine Facies	Interbedded Mudstones and Sandstones		●	○
	Arshan Fm. (K1ba)		Sandy Conglomerates Interbedded with Mudstones and Sandy Mudstones		●	○
First Member (K1ba1)			Gray Mottled Sandy Conglomerates		○	
Paleozoic Basement			Metamorphic and Magma Rocks			

Fig. 2. Cretaceous stratigraphy, depositional systems, source rocks and reservoir rocks of the Baiyinchagan Depression.

positions in the present study. Only some representative samples are discussed in this paper.

3.2. Oil extraction and fractionation

The source rock core samples were first cleaned and then ground into powder (about 200 mesh). The powdered samples (about 50 g each) were Soxhlet extracted with chloroform for 72 h to obtain the source rock extracts (bitumens). The solvent-free extracts, along with the crude oils, were diluted with about 1 ml dichloromethane (DCM), and then deasphalted using about 50 ml hexane. These samples were fractionated on a silica:alumina column using hexane, benzene and methanol as eluants to yield the saturated, aromatic, and resin fractions, respectively. The saturated fractions were further analyzed by GC–FID and GC–MS.

3.3. Extraction and sequential extraction of oil sandstone sidewall cores

The oil-saturated sandstone sidewall cores, collected from wells Da14, Da6 and Da12, were first crushed gently into isolated clasts, and then Soxhlet extracted with dichloromethane:methanol (DCM: MeOH 93:7 v/v) for 72 h. The first extract is considered as the free oil. For sample Da14-1 from well Da14, the solvent extracted clasts were further treated with HCl and HCl:HF for 1 h to remove clay minerals and the grain surfaces. During the treatment with HCl:HF, the kerogen-like matter could be observed in the container. After the acidic treatments, the sample was Soxhlet extracted again with DCM:MeOH (93:7 v/v) for 72 h. The subsequent extract is considered to be the adsorbed oil. The following experimental procedure for the free and adsorbed oils was similar to that for the Soxhlet extracts of the source rocks.

3.4. GC and GC–MS analyses

Gas chromatographic (GC) analysis of the saturated fractions was performed on a HP6890 GC fitted with a 30 m × 0.32 mm i.d. HP-5 column with a film thickness of 0.25 μm and using a nitrogen carrier gas. The GC oven temperature was held initially at 80 °C for 5 min, ramped from 80 to 290 °C at 4 °C/min, and then held at 290 °C for 30 min. Gas chromatographic–mass spectrometric (GC–MS) analysis of the saturated fractions was carried out using a Micromass Platform II interfaced to an HP5890 GC fitted with the same type of column and using helium carrier gas. The GC oven temperature was initially held at 60 °C for 5 min, ramped from 60 to 120 °C at 8 °C/min, from 120 to 290 °C at 2 °C/min, and then held at 290 °C for 30 min.

4. Results and discussion

4.1. Physical properties and gross compositions of crude oils

The densities, viscosities and gross compositions of six representative crude oils from the Daerqi oilfield are shown in Table 1. According to the definition proposed by Martinez (1984) and Liu (1987), oils Da2O1, Da14O3 and Da14O1 belong to the light oil group (densities 0.84–0.87 g/cm³, viscosities 6.7–24 mPa s), while oils Da3O1, Da7O1 and Da12O1 belong to the heavy oil group (densities 0.92–0.97 g/cm³, viscosities 1862.7–433,104 mPa s). The density and viscosity are closely related to the gross composition. The three light oils contain high amounts of saturates (76.1–83.8%), and low total amounts of resins and asphaltenes (4.9–10.7%). In contrast, the three heavy oils contain relatively low amounts of saturates (40.6–61.5%), and

Table 1
Density, viscosity and gross composition for some typical oils from the Daerqi Oilfield

	Groups	Depth (m)	Fm.	Density (g/cm ³)	Viscosity (mPa s)	Gross composition (%)			
						Sat.	Aro.	Res.	Asp.
Da2O1	I (n)	738–748.6	K ₁ bt	0.84	7.1	83.8	11.3	3.8	1.1
Da14O3	I (n)	557–560	K ₁ bd	0.84	6.7	79.2	11.0	9.2	0.6
Da3O1	I (b)	233–241.5	K ₁ bd	0.97	1,862.7	61.5	17.5	10.9	10.1
Da12O1	II (n)	416.6–424	K ₁ bd	0.97	433,104	40.6	13.8	29.7	15.9
Da14O1	III(n)	459–463	K ₁ bd	0.87	24	76.1	13.2	9.7	1.0
Da7O1	III(b)	356–370.4	K ₁ bd	0.92	2134	58.2	18.4	13.6	9.8
Da2 + 12O	Artificial mixing oil (Da2O1:Da12O1 68.7:31.3 wt.)					71.4	12.6	10.1	5.9

(n): non-biodegraded; (b): biodegraded; Fm = Formation; Sat. = Saturates; Aro. = Aromatics; Res. = Resins; Asp. = Asphaltenes.

relatively high total amounts of resins and asphalt-
enes (21.0–45.6%).

4.2. Molecular compositions of crude oils and source rocks

The gas chromatograms and m/z 191 and m/z 217 mass chromatograms of the six representative crude oils and three source rock samples are shown in Figs. 3–7. Selected molecular parameters are provided in Table 2. Oils Da2O1 and Da14O3 contain a

relatively low amount of phytane, with Ph/ n -C₁₈ ratios of 0.94 and 1.02, respectively. Oil Da12O1 contains a high amount of phytane. Oils Da2O1 and Da14O3 have a low Pr/ n -C₁₇ ratio but a high Pr/Ph ratio, in comparison with oil Da12O1. Oil Da14O1 appears intermediate in the abundance of phytane and ratios of Pr/ n -C₁₇, Ph/ n -C₁₈ and Pr/Ph between oil Da2O1 (or Da14O3) and oil Da12O1, but more close to oil Da2O1 (or Da14O3) (Figs. 3a, 3d, 5a and 6a, Table 2). Oils Da3O1 and Da7O1 have completely lost n -alkanes and acyclic

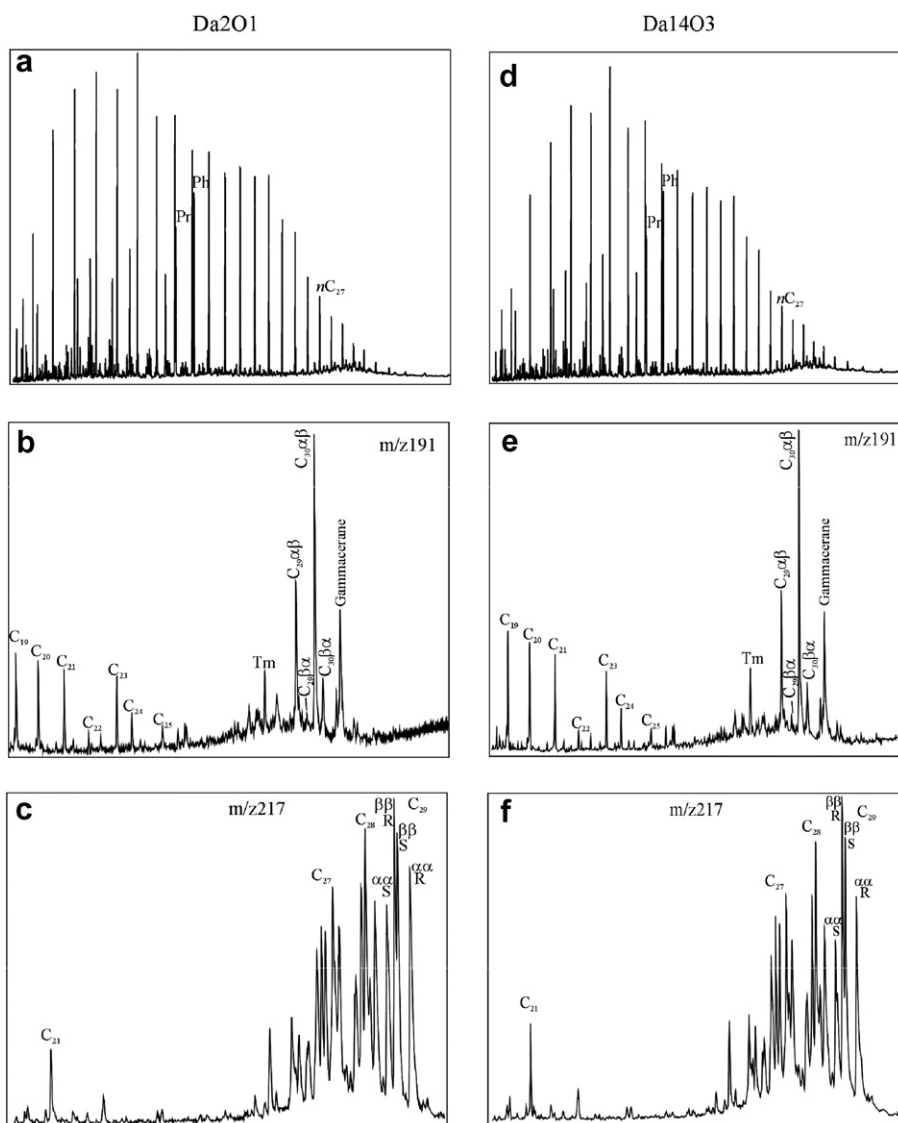


Fig. 3. Gas chromatograms (a and d) and m/z 191 (b and e) and m/z 217 (c and f) mass chromatograms of oils Da2O1 and Da14O3. Peak identifications in b and e, C₁₉–C₂₅: 13β(H)14α(H) isomers of tricyclic terpanes; Tm: C₂₇17α(H)-22,29,30-trisnorhopane; C₂₉αβ: C₂₉17α(H),21β(H)-30-norhopane; C₂₉βα: C₂₉17β(H)21α(H)-30-norhopane; C₃₀αβ: C₃₀17α(H),21β(H)-hopane; C₃₀βα: C₃₀17β(H),21α(H)-hopane.

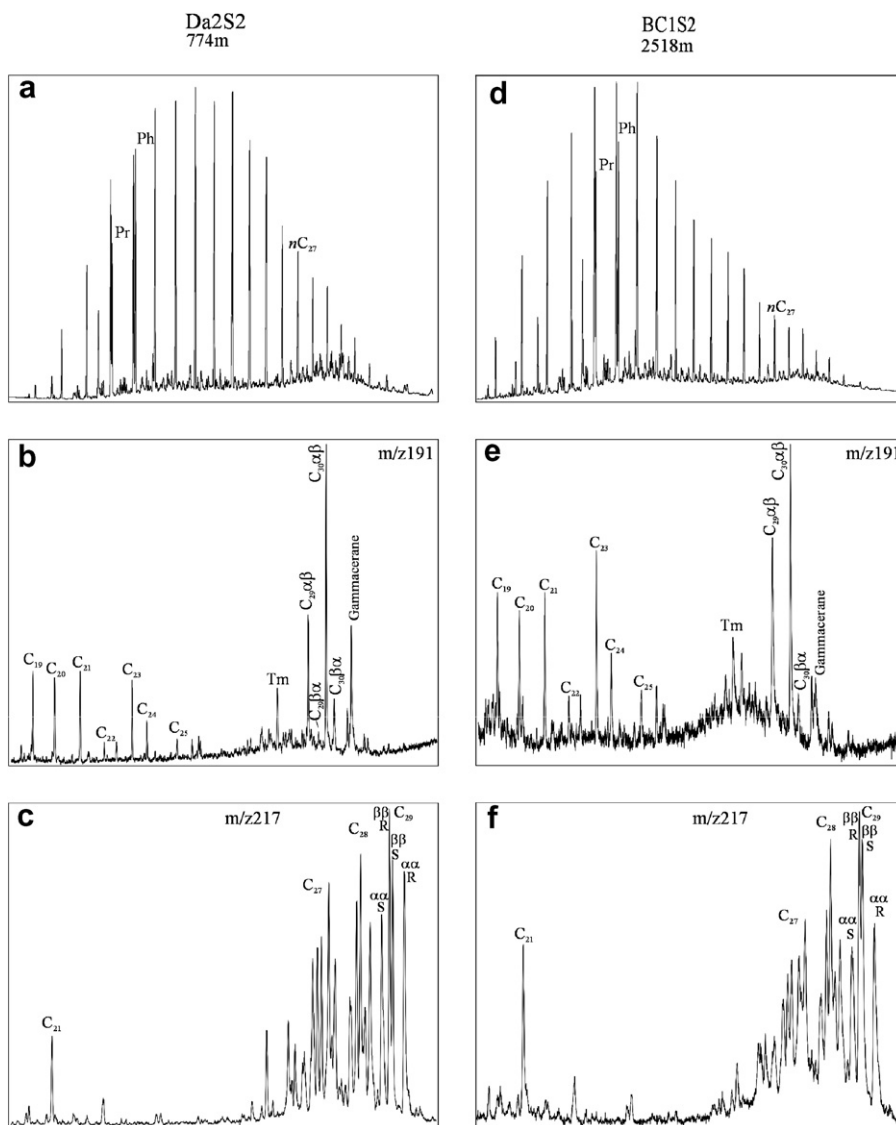


Fig. 4. Gas chromatograms and m/z 191 and m/z 217 mass chromatograms of source rocks Da2S2 within K1bt, and BC1S2 within K1ba2. Peak identifications are as in Fig. 3.

isoprenoids due to heavy biodegradation (Fig. 7). The abundances of pristane and phytane relative to n -alkanes in source rocks Da2S2 and BC1S2, collected from K1bt and K1ba2 respectively, are similar to oils Da2O1 and Da14O3 (Fig. 4a and d, and Table 2). Source rock Da9S1, collected from K1bd1, exhibits similar characteristics in n -alkane and acyclic isoprenoid distributions to oil Da12O1. However, source rock Da9S1 contains an even much higher amount of phytane and exhibits stronger odd–even predominance in n -alkanes than does oil Da12O1 (Fig. 5).

For oils Da2O1, Da14O3 and Da3O1 and source rocks Da2S2 and BC1S2, the ratios of $C_{21}/(C_{21} + \sum C_{29})$ steranes, C_{27} diasteranes/ C_{27} regular steranes, $C_{29}20S/(20R + 20S)$ steranes, $C_{29}\beta\beta/(\alpha\alpha + \beta\beta)$ steranes and C_{23} tricyclic terpane/(C_{23} tricyclic terpane + C_{30} hopane) are relatively high (Table 2, Figs. 3, 4 and 7). In contrast, for oil Da12O1, these ratios are very low (Table 2, Fig. 5). For source rock Da9S1, ratios of C_{23} tricyclic terpane/(C_{23} tricyclic terpane + C_{30} hopane) and $C_{29}20S/(20R + 20S)$ steranes are 0.01 and 0.10, respectively, even lower than those for oil

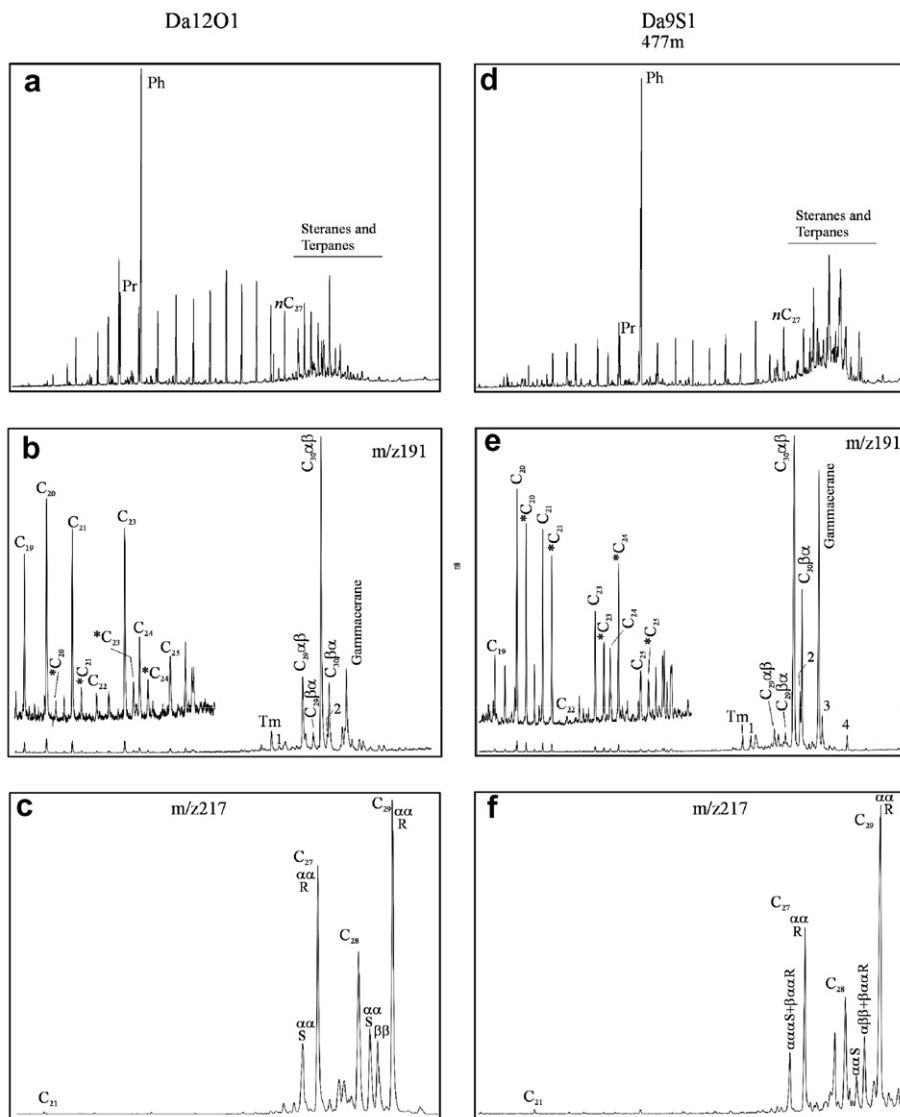


Fig. 5. Gas chromatograms and m/z 191 and m/z 217 mass chromatograms of oil Da12O1 (group II) and source rock Da9S1 within K1bd1. Peak identifications in b and e: *C₂₀–*C₂₅: 13 α (H)14 α (H) isomers of tricyclic terpanes; 1: 17 β (H),22,29,30-trisnorhopane; 2: 17 β (H)21 β (H)-30-norhopane; 3: 17 β (H)21 β (H)-hopane; 4: 17 β (H)21 β (H)-homohopane; the others are as in Fig. 3.

Da12O1. In addition, in comparison with oil Da12O1, source rock Da9S1 contains a high abundance of the less stable 13 α (H)14 α (H)(C₂₀–C₂₅) tricyclic terpane isomers relative to the stable 13 β (H)14 α (H) isomers, and relatively high amounts of 17 β (H),22,29,30-trisnorhopane, 17 β (H)21 β (H)-30-norhopane, 17 β (H)21 β (H)-hopane and 17 β (H)-21 β (H)-homohopane (Fig. 5b and e). For oils Da14O1 and Da7O1, the five maturity ratios are intermediate between oils Da2O1 (or Da14O3) and Da12O1, but closer to oil Da12O1 (Table 2, Figs. 6b,c and 7e,f).

For the biodegraded oils Da3O1 and Da7O1, both the *n*-alkanes and acyclic isoprenoids were almost completely removed while steranes and terpanes were not influenced. The biodegradation extent matches level 4 on the Peters and Moldowan (1993) scale (Huang et al., 2003).

4.3. Source rocks and their thermal maturation histories

Three effective oil-prone source rocks have been identified in the Baiyinchagan Depression (Wang

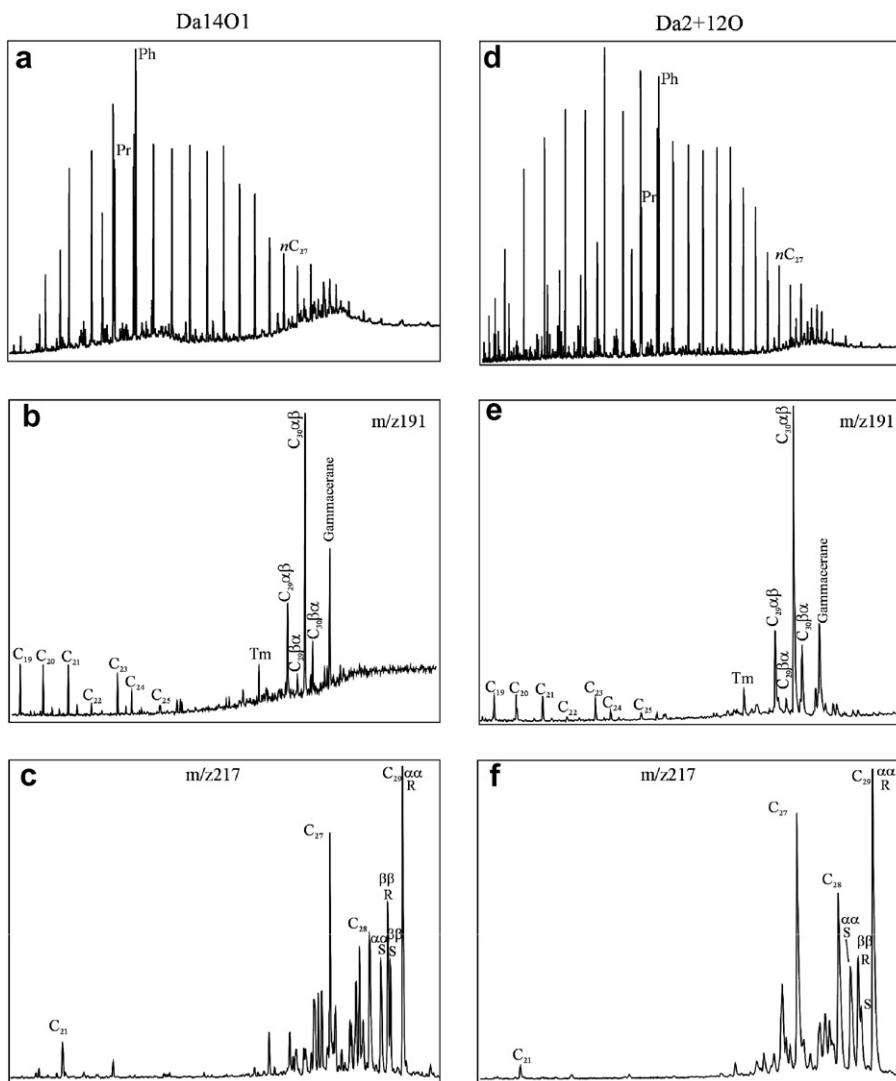


Fig. 6. Gas chromatograms and m/z 191 and m/z 217 mass chromatograms of oil Da1401 (group III) and artificial mixing oil Da2 + 120. Peak identifications are as in Fig. 3.

et al., 1999): (1) shales and dolomitic mudstones located within the first member of the Duhongmu Formation (K1bd1); (2) the Tenger Formation (K1bt); and (3) the second member of the Arshan Formation (K1ba2). This evaluation of source rock potential is based on a large dataset, including total organic carbon contents (TOC), Soxhlet extract amounts, Rock-Eval pyrolysis genetic potential ($S_1 + S_2$), and maturity parameters (vitrinite reflectance R_o %, TAI and T_{max}). Although the third and second members of the Duhongmu Formation (K1bd3, K1bd2) contain mudstones with high TOC values and genetic potential, the thermal maturities of sediments within these two members

are below the level for hydrocarbon generation (Wang et al., 1999).

TOC contents of source rock samples from K1bd1, K1bt and K1ba2 average 2.9%, 1.5% and 1.3%, respectively (Table 3). Rock-Eval and elemental data show that the source rocks of K1bd1 contain mainly type I and type II kerogens, while those of K1bt and K1ba2 contain mainly type II and type III kerogens (Table 4). The source rocks of K1bd1 are immature (i.e. $R_o < 0.5\%$, TAI < 2.5 and $T_{max} < 435$ °C) in the border area of the depression, and at the onset of the oil generation window (i.e. R_o ranging from 0.4% to 0.7%, TAI ranging from 2.6 to 3.0 and T_{max} ranging from 435 to

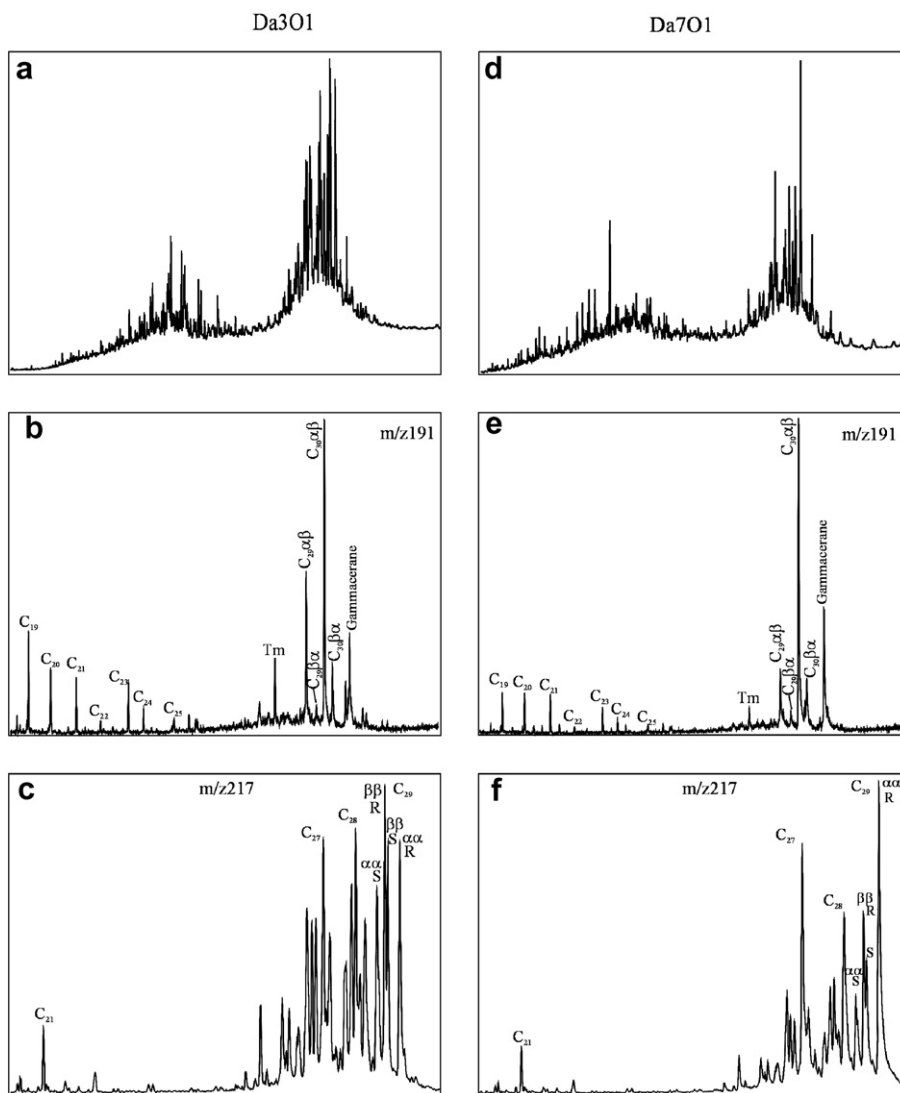


Fig. 7. Gas chromatograms and m/z 191 and m/z 217 mass chromatograms of oils Da3O1 (group I) and Da7O1 (group III). Peak identifications are as in Fig. 3.

440 °C) with burial depths of 865–1430 m in well Baican 1 in the central area of the depression (Fig. 1a). The source rocks of K1bt are moderately mature in the border areas of the depression, in the peak oil generative stage in most areas of the depression and in the condensate generative stage in the central area of the depression. The source rocks of K1ba2 reach the peak oil generative stage in the whole depression, and the gas-condensate generative stage in the central area of the depression (Table 3).

Subsidence of the Baiyinchagan Depression mainly occurred during the Early Cretaceous. Based on the reconstructed burial history and paleo-

thermal gradient, thermal maturation modeling was carried out on source rocks from the well Baican 1, in the central area of the depression (Fig. 1a), using the approach presented by Sweeney and Burnham (1990). As demonstrated in Fig. 8, hydrocarbon generation for all three source rocks occurred during subsidence in the Early Cretaceous. At the end of the Early Cretaceous (Saihantalarian), a major tectonic uplift took place (Gao et al., 1988; Wang et al., 1999). As a result, hydrocarbon generation in all three source rocks ceased due to the substantial decrease in temperature. Although the source rocks were buried again after the uplift, the maximum temperature during the Late Cretaceous

Table 2
Molecular parameters for typical oils and related source rocks

	Groups	Pr/nC ₁₇	Ph/nC ₁₈	Pr/Ph	OEP	1	2	3	4	5
Da2O1	I(n)	0.57	0.94	0.70	1.15	0.052	0.263	0.43	0.49	0.16
Da14O3	I(n)	0.61	1.02	0.70	1.14	0.059	0.335	0.46	0.52	0.17
Da3O1	I(b)	–	–	–	–	0.041	0.259	0.44	0.50	0.11
Da12O1	II(n)	0.78	5.05	0.24	1.11	0.004	0.006	0.25	0.18	0.03
Da14O1	III(n)	0.88	1.73	0.58	1.15	0.044	0.175	0.31	0.37	0.13
Da7O1	III(b)	–	–	–	–	0.031	0.108	0.26	0.34	0.07
Da2 + 12O	mixture	0.60	1.46	0.49	1.14	0.017	0.044	0.28	0.26	0.06
Da2S2	K ₁ bt	0.66	1.05	0.53	1.05	0.059	0.343	0.44	0.50	0.19
BC1S2	K ₁ ba ₂	0.62	0.80	0.70	1.10	0.118	0.211	0.48	0.53	0.26
Da9S1	K ₁ bd ₁	0.76	9.20	0.11	1.58	0.006	0.015	0.10	–	0.01

(1) C₂₁/(C₂₁ + ∑C₂₉) steranes; (2) C₂₇ diasteranes/C₂₇ regular steranes; (3) C₂₉20S/(20R + 20S) steranes; (4) C₂₉ββ/(αα + ββ) steranes; (5) C₂₁ tricyclic terpane/(C₂₁ tricyclic terpane + C₃₀ hopane). Da2S2: source rock samples from K1bt with TOC = 2.0%, collected from well Da2 at 774 m. BC1S2: source rock sample from K1ba2 with TOC = 0.76%, collected from well Baican 1 at 2518 m. Da9S1: source rock sample of K1bd1 with TOC = 4.6%, collected from well Da9 at 477 m. n: non-biodegraded oil; b: biodegraded oil.

Table 3
Organic matter abundances and vitrinite reflectance (R_o, %) of the three source rock formations (see Fig. 2)

	TOC (wt.%) range	TOC (wt.%)	Bitumens (wt.%)	S ₁ + S ₂ (mg/g)	Border areas (R _o , %)	Well Baican-1 (R _o , %)
K1bd1	0.6–7.4	2.9 (96)*	0.22 (18)	12.7 (139)	0.3–0.5 (19)	0.4–0.7 (11)
K1bt	0.3–4.5	1.5 (61)	0.03 (14)	2.3 (81)	0.6–1.0 (11)	0.6–1.0 (4)
K1ba2	0.3–4.5	1.3 (105)	0.05 (18)	4.0 (63)	0.8–1.1 (3)	1.1–1.8 (7)

All data are unpublished and are from the Zhongyuan Oilfield Company, Sinopec; *: number in brackets refers to the number of samples. TOC and S₁ + S₂ data were analyzed on both cores and cuttings, but Soxhlet extract data are for cores only.

Table 4
Kerogen type classification (%) of the three source rocks

	IH-OH diagram				H/C–O/C van Krevelen diagram			
	I	II ₁	II ₂	III	I	II ₁	II ₂	III
K1bd1	25	44	21	10	30	34	16	20
K1bt	11	16	14	59	0	20	40	40
K1ba2	27	3	35	35	6	25	44	25

Data from the Zhongyuan Oilfield Company, Sinopec; IH-OH data are based on Rock-Eval pyrolysis data, while van Krevelen diagram data are based on elemental analysis of kerogens. For source rocks of K1bd1, Rock-Eval analysis of 139 core and cutting samples and elemental analysis of 44 kerogen samples were performed. For source rocks of K1bt, Rock-Eval analysis of 81 core and cutting samples and elemental analysis of 15 kerogen samples were performed. For source rocks of K1ba2, Rock-Eval analyses were performed on 61 core and cutting samples and elemental analyses on 15 kerogen samples.

and Cenozoic Era was significantly lower than that in the Early Cretaceous.

4.4. Oil classification and origins

4.4.1. Origin of mature oils (group I)

Oils Da2O1, Da14O3 and Da3O1 are classified as group I oils. These oils are mature and correlate with source rocks Da2S2 and BC1S2, based on molecular maturity parameters listed in Table 2 (Seifert and Moldowan, 1978, 1986; Mackenzie et al., 1980; Mackenzie, 1984; Peters and Moldo-

wan, 1993). They are, therefore, likely derived from the source rocks within K1bt, or K1ba2, or from both. Wilhelms and Larter (2004) emphasized that all oils are mixtures, with different components charged from source rocks at different temperatures. However, it is unlikely that the group I oils were significantly mixed with immature oil components, such as oil Da12O1. As demonstrated in the gas chromatograms (Fig. 5a), oil Da12O1 contains a high abundance of steranes and terpanes. It can be expected that, even if mixed with a small amount of oil Da12O1, the molecular maturity parameters

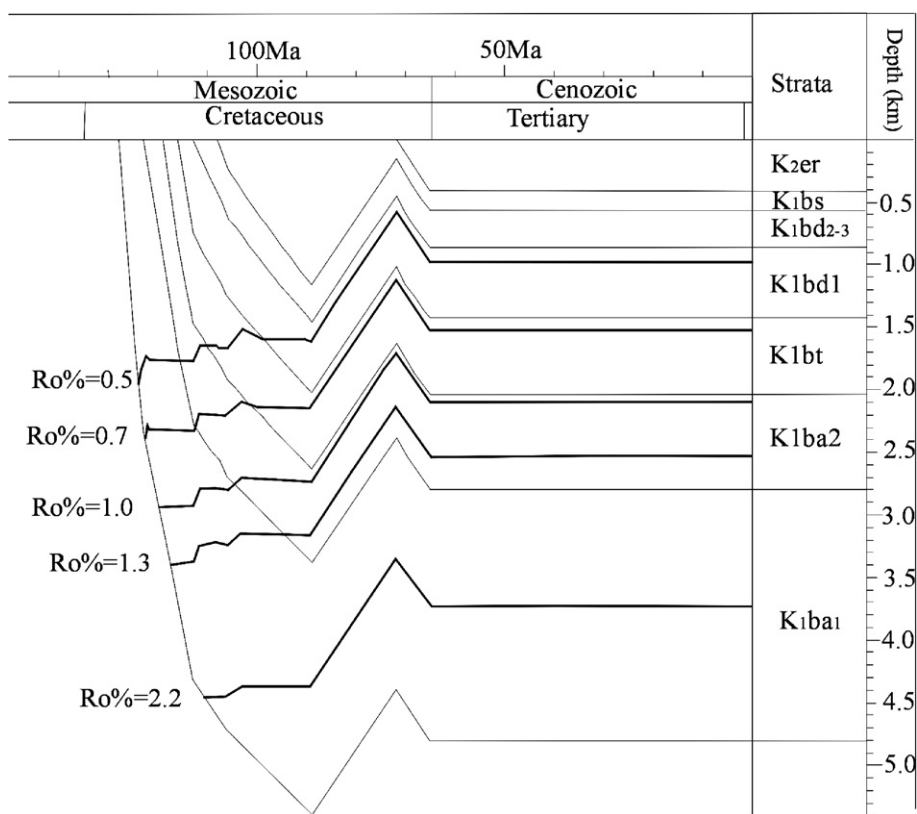


Fig. 8. Modeled burial and thermal maturation histories of Baican 1 well (see Fig. 1a for location).

of the group I oils would be substantially reduced, as discussed later.

4.4.2. Origin of immature oil (group II)

Oil Da12O1 is classified as a group II oil. It is typically immature, based on gross and molecular compositions and physical properties (density and viscosity), and correlates with source rock Da9S1 as discussed above. This oil can only be derived from the source rocks within K1bd1. Oil Da12O1 and source rock Da9S1 were collected from wells Da12 and Da9, respectively, located <1 km apart in the eastern part of the Daerqi oilfield (Fig. 1b). Source rock Da9S1, from a depth of 477 m, is about 55 m deeper than oil Da12O1, from the interval within 416.6–424 m. However, in comparison with oil Da12O1 (Fig. 5b), source rock Da9S1 has a lower maturity, because it contains high abundances of the less stable $13\alpha(\text{H})14\alpha(\text{H})$ isomers relative to the stable $13\beta(\text{H})14\alpha(\text{H})$ isomers for the C_{20} – C_{25} tricyclic terpanes, and high amounts of $17\beta(\text{H})21\beta(\text{H})$ -hopanes (Fig. 5e; Aquino Neto et al., 1983; Chicarelli et al., 1988; Farrimond et al.,

1999; Tuo et al., 1999). Furthermore, source rock Da9S1 contains a higher abundance of phytane and gammacerane and has a greater *n*-alkane odd-even predominance (OEP) than oil Da12O1 (Table 2, Fig. 5), which can be accounted for by both facies and maturity variations (Scalan and Smith, 1970; Fu and Sheng, 1989; Peters and Moldowan, 1993). Therefore, it can be concluded that oil Da2O1 was unlikely charged from the local source rocks, such as Da9S1, but from the source rocks within K1bd1 in the kitchen located down the slope near the central area of the Baiyinchagan Depression, where the maturity for the source rocks within K1bd1 are similar to that of oil Da12O1 (Fig. 1).

Many previous studies have demonstrated that the heavy, highly viscous, non-biodegraded immature oils are usually generated from sulfur-rich kerogen in carbonate/evaporitic or phosphorite source rocks by C–S bond cleavage reactions at low maturities (e.g. Granch and Posthuma, 1974; Tissot, 1984; Tissot and Welte, 1984; Orr, 1986; Fu and Sheng, 1989; Baskin and Peters, 1992; Sinnighe Damsté et al., 1993; di Primio and Horsfield,

1996). It has also been suggested that this type of oil may be generated directly from resins and asphaltenes, rather than from kerogen of sulfur-rich source rocks (e.g. Powell et al., 1975; Powell, 1984; Sinnighe Damsté et al., 1989). As a result, these oils generally contain high amounts of sulfur and their API gravities vary inversely with wt.% sulfur content (e.g. Orr, 1986; Baskin and Peters, 1992). However, the content of sulfur in oil Da12O1 is not high (0.67%). The source rocks within K1bd1 were deposited in a brackish to saline lacustrine environment, which contain a relatively high abundance of carbonate minerals (about 2–25%, mainly dolomite) (Gao et al., 1988; Wang et al., 1999). So far, no source rock bearing sulfur-rich kerogen has been found within K1bd1. The formation mechanism for the group II oils remains unclear, but could be different from that for the previously mentioned oils derived from source rocks with sulfur-rich kerogen.

Oil Da12O1 is similar to tar mats in gross composition, as described by Wilhelms and Larter (1994a,b). However, according to these papers, tar mats usually contain a high content of asphaltenes (20–60%), but have similar molecular compositions to oil legs with high molecular maturity. Therefore, the group II oils in our case are completely different from the tar mats in terms of their molecular and geochemical properties and formation mechanisms.

4.4.3. Origin of oils with intermediate maturity (group III)

Oil Da14O1 is intermediate between oils Da2O1 (group I) and Da12O1 (group II), and is classified

as group III. In physical properties (density and viscosity) and gross composition, oil Da14O1 is closer to oil Da2O1, but is strikingly different from oil Da12O1 (Table 1). However, in terms of sterane and terpene compositions, oil Da14O1 is closer to oil Da12O1, but is substantially different from oil Da2O1 (Table 2, Figs. 3, 5 and 6).

In previous studies, it was suggested that oils Da12O1, Da14O1 and Da7O1 have a similar maturity based on sterane maturity parameters, and therefore, belong to the same genetic group derived from the source rocks within K1bd1 (Wang et al., 1999; Zhang et al., 1999; Huang et al., 2003). These authors believed that oils Da12O1 and Da14O1 could have had similar chemical and physical properties (i.e. gross composition, density and viscosity), and ascribed the high amount of polar components and the high density and viscosity of current oil Da12O1 mainly to post-generation alteration processes, such as oil evaporation after accumulation (Zhang et al., 1999), or water-washing, in combination with evaporation and leakage (Huang et al., 2003).

Oil brine data obtained so far from the Daerqi oilfield do not support the proposition that group II oil columns have suffered any significant fresh water washing. As listed in Table 5, the salinity and Cl⁻ content for oilfield brines are generally high, ranging from 16,171–140,230 ppm and 8530–84,115 mg/l, respectively. For the biodegraded group I oil columns in well Da3 and Da6, the brine salinity and Cl⁻ contents are relatively low, 16,171–30,425 ppm and 8530–16,404 mg/l, respectively,

Table 5
Subsurface water chemistry in the Baiyinchagan Depression

Well	Fm.	Depth (m)	Property	Salinity (ppm)	Cl ⁻ (mg/l)
Baicán 1	K1bd1	1081–1123	Water	108,087	63,786
Baicán 1	K1bt	1256–1321	Water	95,270	55,813
Da2	K1bt1	738.6–764.4	Group I(n)	140,230	84,115
Da3	K1bt	233–241.5	Group I(b)	18,989	10,514
Da3	K1bt	252–267	Group I(b)	20,076	11,043
Da4	K1bt	758.1–760.1	Group I(n)		61,401
Da4	K1bt	592.9–594.8	Group I(n)	112,189	67,807
Da4	K1bt	579–596	Group I(n)	110,069	65,581
Da6	K1ba	433.4–436.4	Group I(b)	21,849	8990
Da6	K1ba	433.4–457	Group I(b)	30,425	16,404
Da6	K1bd1	239.4–263.6	Group I(b)	16,171	8530
Da7	K1bd1	355.8–370.4	Group III(b)		61,448
Da8	K1bd1	569.8–575.6	Group II(n)	87,039	50,203
Da9	K1bd1	467.3–508.8	Group II(n)		42,975

Data from the Zhongyuan Oilfield Company, Sinopec; water: from water column, the others: from oil columns; n: non-biodegraded oil; b: biodegraded oil.

possibly demonstrating that fresh water has percolated into these columns. In contrast, for non-biodegraded group I oil columns in wells Da2 and Da4 and group II oil columns in wells Da8 and Da9, the brine salinity and Cl^- content are strikingly high, 87,039–140,230 ppm and 42,975–84,115 mg/l, respectively, indicating that the possibility of fresh water washing can be excluded for these columns. In fact, polar components with high aqueous solubility are more easily removed from oils than saturated hydrocarbons with low aqueous solubility during water washing (Price, 1976). The results of the experimental study by Kuo (1994) did not support substantial decrease of saturates and increase of polar components of the residual oils after water washing. Therefore, it is difficult to account for the gross composition of oil Da12O1 using water washing. Furthermore, the biodegraded oils Da3O1 and Da7O1 are shallower, and therefore, could be much easier to evaporate and leak than oil Da12O1. The high proportion of saturated fractions and the low viscosity of biodegraded oils Da3O1 and Da7O1 relative to oil Da12O1 do not support the possibility that evaporation and leakage are the important factors influencing the chemical and physical properties of crude oils in this region.

In addition to substantial variations in gross composition, density and viscosity, several significant differences in molecular composition can be also observed between oils Da12O1 and Da14O1:

- (1) The Pr/Ph ratio is much lower while the Ph/ $n\text{-C}_{18}$ ratio is much higher in oil Da12O1 than oil Da14O1.
- (2) The ratios of $\text{C}_{21}/(\text{C}_{21} + \sum\text{C}_{29})$ steranes, C_{27} diasteranes/ C_{27} regular steranes and C_{21} tricyclic terpane/ $(\text{C}_{21}$ tricyclic terpane + C_{30} hopane) are significantly lower in oil Da12O1 than oil Da14O1.
- (3) The ratios of $\text{C}_{29}20\text{S}/(\text{R} + \text{S})$ steranes and $\text{C}_{29}\beta\beta/(\alpha\alpha + \beta\beta)$ steranes are relatively lower in oil Da12O1 than in oil Da14O1, and
- (4) Considerable amounts of $\alpha\beta\beta 20\text{R}$ and 20S C_{27} steranes can be observed in oil Da14O1, whereas these components are below the detection level in oil Da12O1 (Figs. 5a–c and 6a–c; Table 2).

These results demonstrate that the maturity of oil Da14O1 is significantly higher than oil Da12O1. Therefore, oil Da14O1 could be a mixture of oils like Da12O1 and Da2O1.

As demonstrated in the reservoir cross section (Fig. 1d), three oil columns have been found within K1bd1 in well Da14. Oil Da14O1 was collected from the first (shallowest) column, while mature oil Da14O3 was collected from the third (deepest) column. Oils from the second column have not been analyzed yet. These three oil columns are bounded by two faults that cut all the three source rocks of K1bd1, K1bt and K1ba2. These reservoir geological features also strongly support the contention that oil Da14O1 is very likely a mixture of mature oil such as Da2O1 or Da14O3 and immature oil such as Da12O1. Biodegraded oil Da7O1 contains a higher amount of saturates than oil Da12O1 and is correlated much better with oil Da14O1 than with oil Da12O1 in terpane and sterane mass chromatograms. These results demonstrate that oil Da7O1 formed from the biodegradation of group III oil (such as Da14O1), rather than group II oil (such as Da12O1).

4.4.4. Artificial oil mixing experiment

In the present study, an artificial oil mixing experiment was carried out using Da2O1 (68.7%) and Da12O1 (31.3%). The mixed oil (Da2 + 12O) is similar to oil Da2O1 in the gross composition and gas chromatograms of saturates (Table 1 and Figs. 3a and 6d), whereas it is similar to oil Da12O1 in the terpane and sterane mass chromatograms (Table 2 and Figs. 5b,c and 6e,f). In comparison with oil Da14O1, Da2 + 12O contains a relatively lower amount of the saturated fraction and has a lower molecular maturity (Tables 1 and 2, Fig. 6). These results suggest that oil Da14O1 could contain more mature oil such as Da2O1 (>70%) and less immature oil such as Da12O1 (<30%) than the mixed oil Da2 + 12O. The observation that oil Da14O1 has relatively higher Pr/ $n\text{-C}_{17}$ and Ph/ $n\text{-C}_{18}$ ratios than the mixed oil Da2 + 12O could be ascribed to the apparently greater evaporation of light hydrocarbons from the former relative to the latter during storage (Fig. 6a and d; Table 2). However, oil Da14O1 has a high Pr/Ph ratio in comparison with Da2 + 12O, although this ratio decreases with increasing evaporation extent. This result also suggests that oil Da14O1 contains more mature oil components than does the mixed oil Da2 + 12O.

4.4.5. Sequential extraction

Sequential extraction (Wilhelms et al., 1996) was performed on an oil sandstone sidewall core Da14-1 to reconstruct the filling process of the reservoir of the oil Da14O1. When the initial oil components

entered the reservoir sandstone, the polar components (resins and asphaltenes) preferentially reacted with and were irreversibly adsorbed by the mineral surface (especially clay surfaces). Therefore these adsorbed components from the initial oil were unlikely replaced by those from the later charging oil. The adsorbed polar components themselves inevitably entrapped some non-polar saturates into their network. As the polar compounds are firmly bound to the mineral surface (e.g. via hydrogen bonding) the hydrocarbons trapped between the bonded polar compound and the mineral surface are also fixed. Several previous studies have demonstrated that the adsorbed oil fractions, obtained by sequential extraction, retain more molecular characteristics of the initial oils than do the free oil fractions in the pore system of the reservoir sandstones (Wilhelms et al., 1996; Schwark et al., 1997; Pan and Yang, 2000; Pan et al., 2005). For this sidewall core, the adsorbed oil Da14-1b is characterized by low Ph/ n -C₁₈ ratios but high ratios of Pr/Ph, C₂₇ diasteranes/C₂₇ regular steranes, C₂₉20S/(R + S) steranes and C₂₉ββ/(αα + ββ) steranes, in comparison with the free oil Da14-1a (Table 6; Fig. 9). It appears that the adsorbed oil Da14-1b contains more mature oil such as Da2O1 than does the free oil Da14-1a. This result suggests that the mature oil such as Da2O1 entered the reservoir first, and then the immature oil such as Da12O1 followed. This sequence is consistent with that of oil generation and migration from the three source rocks in this region. Compositional fractionation can be also induced by selective adsorption. Our previous studies (Pan and Yang, 2000; Pan et al., 2005), as well as the early studies on geochromatography effects induced by oil migration (Seifert and Moldowan, 1978, 1981, 1986), demonstrated that the oil components adsorbed by minerals are rich in regular steranes relative to diasteranes, and 5α,14α,17α isomers relative to 5α,14β,17β isomers of C₂₇–C₂₉ steranes, exactly opposite to the compositional variations observed between the adsorbed oil and free oil of sidewall core Da14-1. Therefore, the molecular variations revealed by sequential extraction on this sidewall core were unlikely to have been induced by selective adsorption, but reflect the molecular variations of the charging oils during the reservoir filling process.

In summary, crude oils in Daerqi oilfield can be classified into three groups: (1) group I oils include both the non-biodegraded ones, such as Da2O1 and Da14O3, and biodegraded ones, such as Da3O1, being derived from the mature source rocks

Table 6
Amounts and gross compositions of extracts from the oil sandstone sidewall cores

Sample no.	Depth (m)	wt. (g)	Extract (mg)	Extract (mg/g)	Gross composition (%)				Pr/ n C ₁₇	Ph/ n C ₁₈	Pr/Ph	1	2	3	4	5
					Sat.	Aro.	Res.	Asp.								
Da14-1a	462	8.4	61.4	7.3	50.9	8.7	38.2	2.2	1.16	1.97	0.52	0.055	0.178	0.27	0.40	0.20
Da14-1b	462	8.4	6.8	0.8	3.1	1.3	95.6	0.84	1.11	0.84	0.057	0.221	0.39	0.46	0.19	
Da6-1	180	10.6	141.0	13.2	52.6	15.9	22.9	8.6	–	–	–	0.087	0.392	0.51	0.58	0.37
Da6-2	259	2.8	185.6	67.0	47.6	11.1	30.2	11.1	–	–	–	0.049	0.334	0.50	0.56	0.18
Da6-3	273.5	7.0	56.1	8.0	34.9	6.7	56.5	1.9	0.68	2.74	0.29	0.017	0.018	0.22	0.22	0.06
Da6-4	427.3	11.0	244.3	22.1	32.1	12.7	38.7	16.5	–	–	–	0.039	0.276	0.49	0.53	0.10
Da6-5	435	4.0	30.7	7.6	29.9	14.8	40.1	15.2	–	–	–	0.021	0.265	0.49	0.50	0.06
Da12-1	375.7	6.4	451.9	70.7	16.3	4.5	75.8	3.4	0.81	5.95	0.22	0.003	0.007	0.23	0.17	0.02
Da12-2	426	4.7	343.5	72.4	42.7	14.6	32.2	10.5	–	–	–	0.028	0.147	0.31	0.40	0.07
Da12-3	440	8.4	793.5	117.7	41.4	11.3	37.3	10.0	–	–	–	0.065	0.145	0.33	0.45	0.17
Da12-4	454.7	7.5	884.3	125.6	15.4	4.1	61.2	19.3	0.77	5.36	0.22	0.003	0.006	0.24	0.18	0.03
Da12-5	465	2.6	320.2	94.8	13.0	3.4	79.3	4.3	0.77	5.16	0.21	0.004	0.009	0.24	0.17	0.04

Da14-1a: free oil; Da14-1b: adsorbed oil; the others: free oil. Da6-4 and Da6-5: from K1ba; the others: from K1bd; Abbreviations as in Table 1; 1–5: as in Table 2.

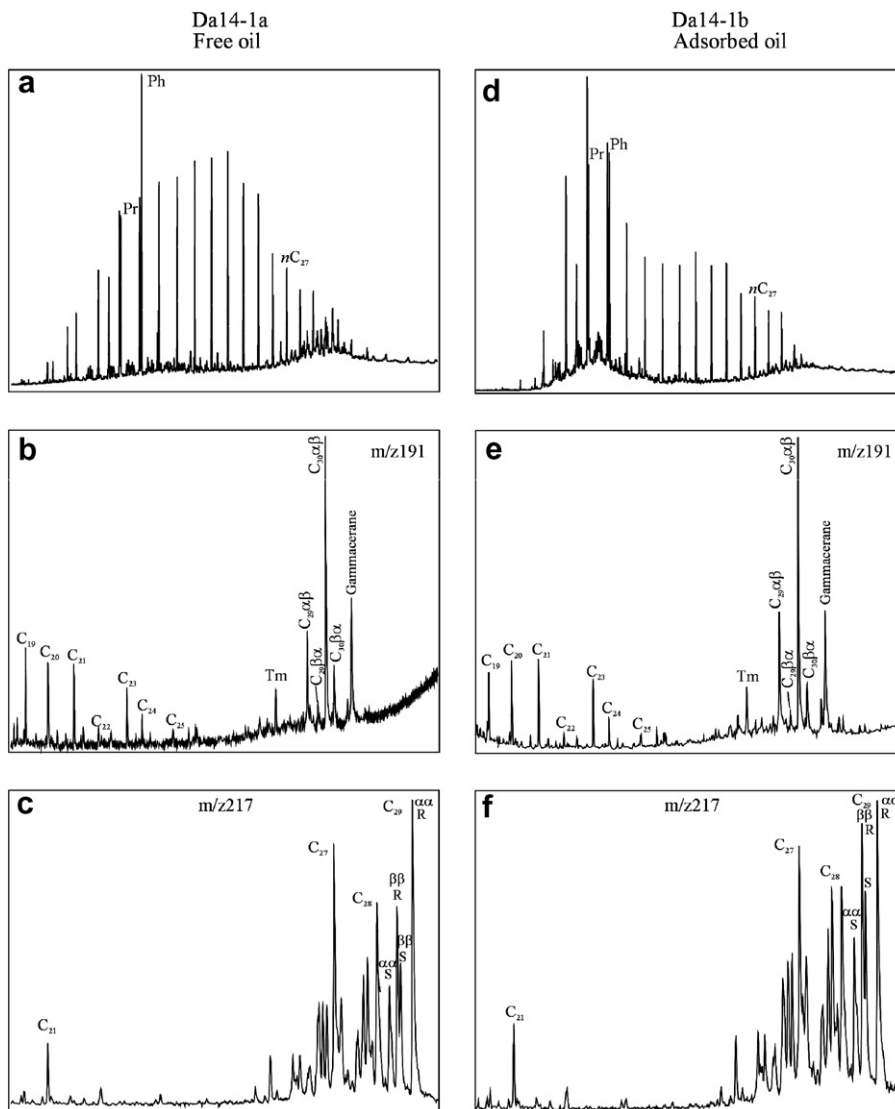


Fig. 9. Gas chromatograms and m/z 191 and m/z 217 mass chromatograms of the free and adsorbed oils from oil sandstone sidewall core Da14-1. Peak identifications are as in Fig. 3.

within K1bt and K1ba2; (2) group II oils include only the non-biodegraded ones, such as Da12O1, being derived from the immature source rocks within K1bd1; and (3) group III oils include both the non-biodegraded ones, such as Da14O1, and biodegraded ones, such as Da7O1, being mixtures with a dominance of group I (>70%) and a minor proportion of group II (<30%).

4.5. Oil biodegradation

4.5.1. Biodegradation on oil columns of well Da6

The Da6 well is located on the upper side of the slope, in the southeastern part of the Daerqi Oilfield

(Fig. 1). Five oil sandstone sidewall cores were collected and systematically analyzed within the interval 180–435 m (Table 6, Fig. 10). As demonstrated by the gas chromatograms of the saturated fraction, oil components are heavily biodegraded in sidewall cores Da6-1, Da6-2, Da6-4 and Da6-5 while they are almost unaltered in sidewall core Da6-3 (Fig. 10). Oil components in the four biodegraded sidewall cores apparently belong to the biodegraded group I, whereas those in the non-biodegraded one (Da6-3), belongs to group II.

As demonstrated in Table 6, the non-biodegraded sidewall core Da6-3 contains a high amount of resins but low amounts of aromatics and

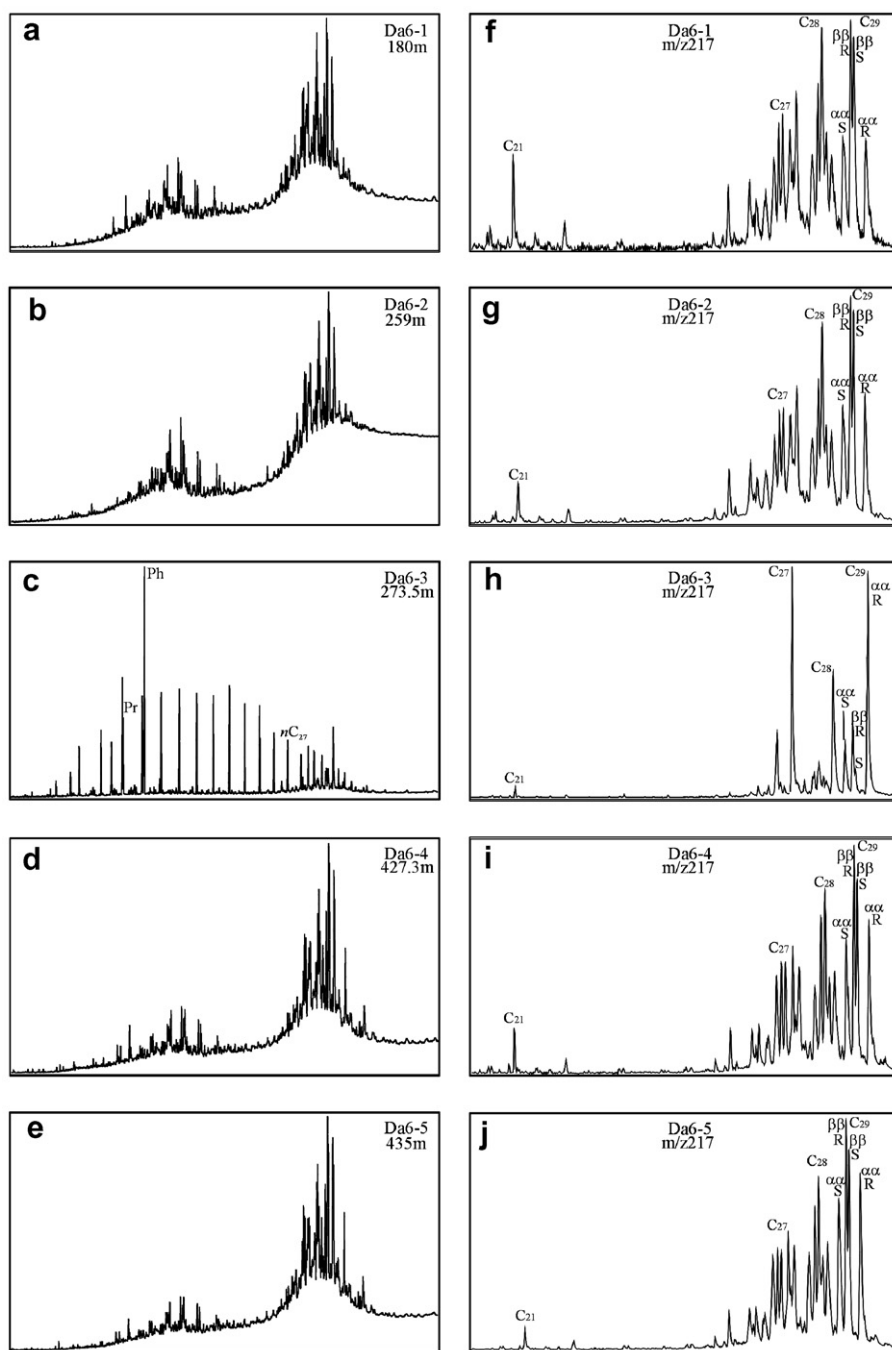


Fig. 10. Gas chromatograms and m/z 217 mass chromatograms of the free oils from oil sandstone sidewall core samples in Da6 well.

asphaltenes in comparison with the four biodegraded ones. The non-biodegraded core Da6-3 has a lower amount of saturated fraction than in the biodegraded cores Da6-1 and Da6-2, but higher than that in the biodegraded cores Da6-4 and Da6-5.

4.5.2. Biodegradation on oil columns of well Da12

The Da12 well is located on the lower portion of the slope in the northeastern part of the Daerqi oil-field (Fig. 1). Five oil sandstone sidewall cores were collected and systematically analyzed within the interval 375.7–465 m (Table 6, Fig. 11). The gas

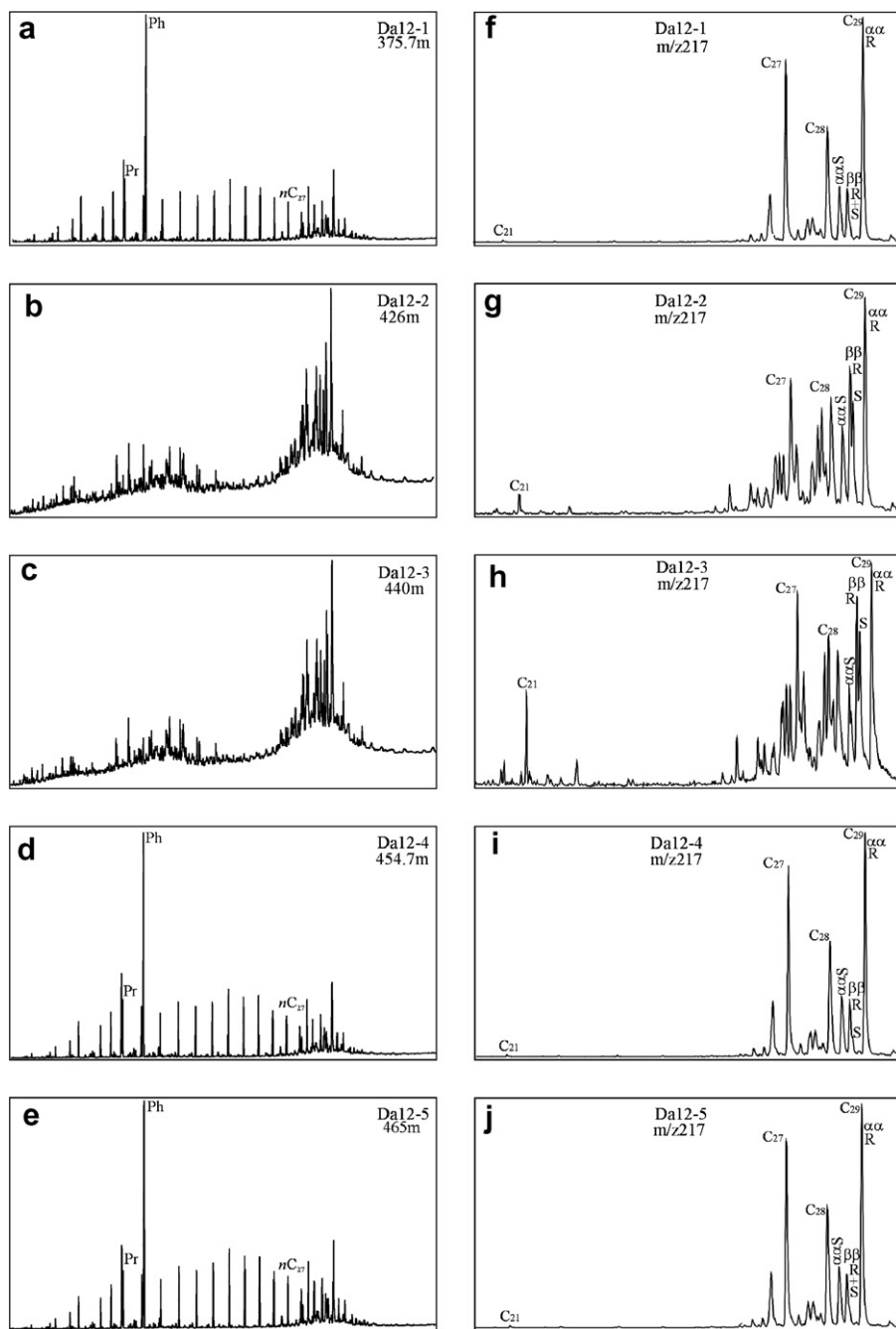


Fig. 11. Gas chromatograms and m/z 217 mass chromatograms of the free oils from oil sandstone sidewall core samples in Da12 well.

chromatograms of the saturated fractions demonstrate that oil components are heavily biodegraded in sidewall cores Da12-2 and Da12-3 whereas they remain almost unaltered in sidewall cores Da12-1, Da12-4 and Da12-5 (Fig. 11). The three non-biodegraded oils contain components typical of group II oils (Figs. 5a–c, 11a, d–f and i,j), whereas the two biodegraded sidewall core oil contain components

of the biodegraded group III (Figs. 7d–f, 11b,c and g,h). Wells Da7 and Da12 are located in the same reservoir within a distance of <1 km (Fig. 1b). However, biomarker parameters show that the maturity of oil in sidewall core Da12-3 is substantially higher than that of oil Da7O1 (Tables 2 and 6, Figs. 7e,f and 11h). This result suggests that oil in sidewall core Da12-3 contains more components of group I than

does oil Da7O1, and it belongs to an intermediate type between groups I and III.

As demonstrated in Table 6, the non-biodegraded cores Da12-1, Da12-4 and Da12-5 contain a high amount of resins but low amounts of saturates and aromatics in comparison with the biodegraded cores Da12-2 and Da12-3.

4.5.3. Factors influencing oil biodegradation

Oil reservoirs in the Daerqi oilfield have suffered deep burial and subsequently major uplift at the end of the Early Cretaceous (Gao et al., 1988; Dou et al., 1998; Wang et al., 1999; Huang et al., 2003). Wilhelms et al. (2001) suggested that petroleum reservoirs are sterilized by heating to a temperature around 80–90 °C during deep burial, inactivating hydrocarbon-degrading organisms that occur in the deep biosphere. An important implication of this sterilizing model is that following uplift, recharge of fluid and/or microorganisms from the surface and migration of microorganisms into pasteurized deep subsurface petroleum reservoirs are insignificant (Head et al., 2003). If this palaeopasteurization model is applied to interpret the phenomenon of oil biodegradation within wells Da6 and Da12, it would be suggested that the biodegraded oil columns were charged before pasteurization during burial at low temperature, and then biodegradation occurred till temperatures up to 80–90 °C were reached, while the non-biodegraded oil columns were charged after pasteurization during burial at temperatures higher than 80–90 °C. This interpretation may be sound for well Da6 under the consideration that group II oils within the non-biodegraded columns were derived from the younger source rocks within K1bd1, and entered the reservoirs later than did group I oils within the biodegraded oil columns, which were derived from the older source rocks within K1bt and/or K1ba2. However, this interpretation appears unreasonable for well Da12 under the consideration that group III oils within the biodegraded oil columns are mixtures of groups I and II oils. Furthermore, all three oil groups entered the reservoirs before the major uplift because oil generation from all source rocks ceased and the migration for the highly viscous group II oils was unfavorable at low temperature after the major uplift. Therefore, it is unlikely that the non-biodegraded group II oils entered the reservoir very recently.

The measured fluid pressure coefficient (fluid pressure/hydrostatic pressure ratio) of reservoirs

in the Daerqi oilfield ranges from 1.0 to 1.1. As the density of both the biodegraded oils and the non-biodegraded oils in wells Da6 and Da12 is high, it is difficult to determine the communication of oil columns within the reservoirs based on fluid pressure. The communication between oil columns can be evaluated using geochemical data. For example, non-biodegraded oil Da12O1 (group II) and sidewall core Da12-2 (containing biodegraded group III oil) are very close, collected from the interval within 416.6–424 m and at 426 m, respectively. If these two oil columns are connected, they should be completely mixed with each other by diffusion. Although the diffusion rate could be extremely low within the group II oil column, it would have been very high within the group III oil column before biodegradation. Furthermore, the reservoir rocks within K1bd1 are generally of high quality, with porosity up to 20%. The amount of oil in the five sidewall cores from well Da12 ranges from 70.7 to 126 mg/g (Table 5). This result indicates that the porosity of these five cores to be in the range 14–25%.

Recent studies have suggested that the site of most biodegradation is at the base of the oil column. Therefore, the diffusive transport of oil components to the oil–water contact could be an important factor in controlling biodegradation rates (e.g. Head et al., 2003; Larter et al., 2003). The diffusion coefficient is bound to be significantly lower in group II oil columns with high viscosity than in groups I and III oil columns with low viscosity (e.g. Larter et al., 2003). Oil columns in well Da12 appear to be in contact directly with the under-seals and the oil–water contacts are located down the flank between wells Da9 and Da8 (Fig. 1e). This reservoir geometry is apparently disadvantageous for oil biodegradation. Earlier studies suggested that the exposure of oil reservoirs to percolating meteoric waters could be critical for the oil biodegradation (e.g. Evans et al., 1971; Bailey et al., 1973; Tissot and Welte, 1984; Peters and Moldowan, 1993). Recent studies have demonstrated that although water flow is not essential, it would, however, help mineral dissolution and nutrient supply, promoting microbial activity (e.g. Larter et al., 2003; Head et al., 2003). The Daerqi Oilfield is currently shallow and the brine data demonstrate that fresh water may have percolated into the biodegraded oil columns in well Da3 and Da6, based on relatively low salinities and Cl⁻ content (Table 5). However, the brine data also exclude the possibility of fresh water washing

through the biodegraded group III oil column in well Da7 and non-biodegraded group II oil columns in wells Da9 and Da8, based on strikingly high salinity and Cl^- content (Table 5).

Group II oils have been also found in wells Da9, Da11, Da13 and Da15, in addition to wells Da6 and Da12 (Fig. 1b). None of the group II oils found so far in the Daerqi Oilfield is biodegraded. There are two possible models for oil charging and biodegradation in this oilfield. The first is that both the oil charging and biodegradation occurred during burial in the Early Cretaceous. Group I oil entered the reservoirs within the Duhongmu Formation (K1bd) at low temperature ($<80^\circ\text{C}$), and then biodegradation occurred. When group II oil arrived, reservoirs within K1bd were still at temperatures lower than that required for pasteurization. Some group II oils entered the biodegraded group I oil columns and were subsequently biodegraded, forming the biodegraded group III oils, while some others entered the fresh sandstones (water columns), and remained non-biodegraded. The group II oils were preserved from the biodegradation because of the short duration from oil charging to reservoir pasteurization, in combination with high viscosity and low diffusion coefficient. The second model is that the oil charging of groups I and II oils occurred during the burial process while the biodegradation occurred mainly during and after the major uplift at the end of the Early Cretaceous. In the second model, either the reservoirs suffered temperatures lower than that required for pasteurization during burial, and biodegradation continued and speeded up due to temperature decrease after the major uplift, or the reservoirs were sterilized during burial and then hydrocarbon-degrading bacteria recolonized them due to fresh water percolation after the major uplift. The group II oil columns are resistant to biodegradation, possibly due to low diffusion coefficients for hydrocarbons and isolation from meteoric water percolation as indicated by the brine data (Table 5). However, the hypothesis of recolonization by a microbial community in sterilized reservoirs is inconsistent with recent studies on oil biodegradation (Wilhelms et al., 2001; Head et al., 2003; Larter et al., 2003).

5. Conclusions

Oils in Daerqi oilfield vary greatly in gross properties (e.g., viscosity and gross compositions) and in molecular parameters. In the present study, three

genetic oil groups have been identified. Group I oils are mature and were derived from the deeply buried source rocks within the Tengger Formation (K1bt) and the second Member of the Arshan Formation (K1ba2) of Early Cretaceous age. Group II oils are immature to marginally mature, and were derived from the shallowly buried source rocks within the first Member of the Duhongmu Formation (K1bd1) of Early Cretaceous age. Group III oils appear to be the mixture of groups I and II, and dominated by group I. The result of oil mixing experiments demonstrates that oil Da14O1, the representative of group III, is composed of more than 70% group I oil components and less than 30% group II oil components. The result of sequential extraction on oil sandstone sidewall core suggests that group I oils entered the reservoir of Da14O1 first, and then group II oils followed.

Viscosity is low for the non-biodegraded groups I and III oils, but is very high for the non-biodegraded group II oils. The group III oils are similar to group I oils in gross properties (e.g., gross composition and viscosity), whereas they are similar to group II oils in molecular maturity parameters.

The oil reservoirs are currently at shallow depths ($<800\text{ m}$), and some groups I and III oils have been heavily biodegraded in this region. However, group II oils are not affected by biodegradation, even though some are interbedded with the heavily biodegraded groups I or III oils, possibly due to low diffusion coefficients for hydrocarbons and isolation to meteoric water percolation. The brine data demonstrate that the biodegraded group I oil columns in well Da3 and Da6 may have been invaded by meteoric water, while the biodegraded group III oil column in well Da7 and all the non-biodegraded oil columns are unlikely to have been flooded by meteoric water.

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